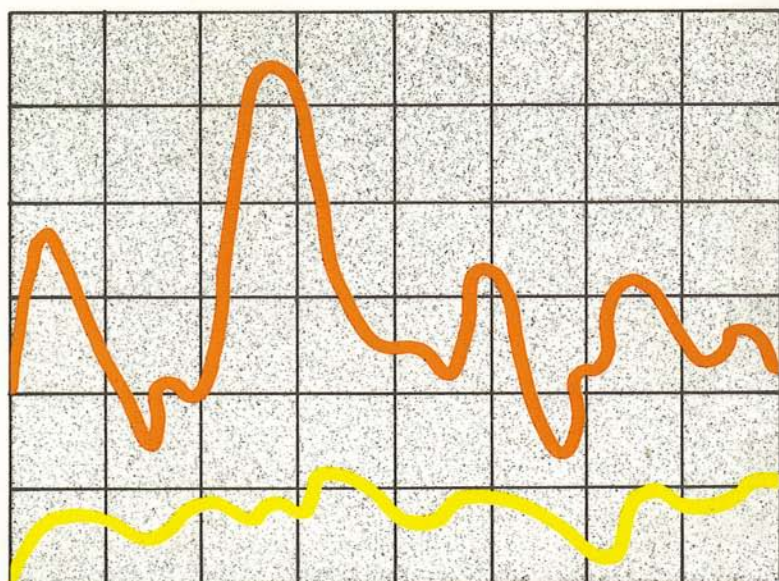# THE PROPERTIES OF
GASES & LIQUIDS

FOURTH EDITION

ROBERT C. REID

JOHN M. PRAUSNITZ

BRUCE E. POLING

THE PROPERTIES OF
GASES & LIQUIDS

A comprehensive and critical survey of the most reliable estimating methods in use today—plus property values for more than 600 pure chemicals.

This highly regarded reference has been completely revised to bring you the latest developments in estimating the properties of gases and liquids.

An invaluable aid to engineers and scientists, it is the only book in the field to give you a critical analysis of existing estimating methods as well as instantly usable practical recommendations for estimating . . .

. . . Physical properties when experimental data are not available, for example, critical constants, vapor pressures, viscosities, thermal conductivities, diffusion coefficients, and surface tension

. . . Thermodynamic properties of gases and liquids, both pure and mixtures, including densities, enthalpies, entropies, fugacity coefficients, and heat capacities

. . . Vapor-liquid and liquid-liquid equilibria as needed in separation operations such as distillation, absorption, and extraction

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The Properties of Gases and Liquids

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Fourth Edition

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Preface

Reliable values of the properties of materials are necessary for the design of industrial processes. An enormous amount of data has been collected and correlated over the years, but the rapid advance of technology into new fields seems always to maintain a significant gap between demand and availability. The engineer is still required to rely primarily on common sense, experience, and a variety of methods for estimating physical properties.

This book presents a critical review of various estimation procedures for a limited number of properties of gases and liquids: critical and other pure component properties, PVT and thermodynamic properties of pure components and mixtures, vapor pressures, and phase-change enthalpies, standard enthalpies of formation, standard Gibbs energies of formation, heat capacities, surface tensions, viscosities, thermal conductivities, diffusion coefficients, and phase equilibria. Comparisons of experimental and estimated values are normally shown in tables to indicate reliability. Most methods are illustrated by examples.

The procedures described are necessarily limited to those which appear to the authors to have the greatest validity and practical use. Wherever possible, we have included recommendations delineating the best methods for estimating each property and the most reliable techniques for extrapolating or interpolating available data. Recommended methods are often illustrated by detailed examples.

Although the book is intended to serve primarily the practicing engineer, especially the process or chemical engineer, other engineers and scientists concerned with gases and liquids may find it useful.

The first edition of this book was published in 1958, the second in 1966, and the third in 1977. Each revision is essentially a new book, because many estimation methods are proposed each year and, over an 8- to 10-year span, most earlier methods are modified or displaced by more accurate or more general techniques. Most new methods are still empirical in nature, although there are often theoretical bases for the correlation;

whenever possible, the theory is outlined to provide the user with the foundation of the proposed estimation method.

The data bank, Appendix A, is now about 15 percent larger than that in the third edition. More important, many estimated quantities in the earlier version have now been replaced by experimental results.

Many colleagues and students have contributed data, advice, examples, or illustrative calculations; we are grateful to them all. For their helpful contributions, we want to record our thanks to C. Baroncini, M. R. Brulé, R. Lopes Cardozo, T. -H. Chung, J. H. Dymond, W. Hayduk, J. B. Irving, J. D. Isdale, D. T. Jamieson, K. G. Joback, J. Kestin, D. Klingenberg, D. Kyser, G. Latini, L. L. Lee, K. Lucas, D. Reichenberg, R. L. Rowley, A. S. Teja, T. P. Thinh, R. Topliss, A. Vetere, and J. Wong.

Special thanks are due to D. Ambrose for contributions to the data bank and to estimation methods for critical constants and to J. McGarry for extensive help in regression of vapor-pressure data.

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The Estimation
of Physical Properties

1-1 Introduction

The structural engineer cannot design a bridge without knowing the properties of steel and concrete. Similarly, scientists and engineers often require the properties of gases and liquids. The chemical or process engineer, in particular, finds knowledge of physical properties of fluids essential to the design of many kinds of industrial equipment. Even the theoretical physicist must occasionally compare theory with measured properties.

The physical properties of every substance depend directly on the nature of the molecules of the substance. Therefore, the ultimate generalization of physical properties of fluids will require a complete understanding of molecular behavior, which we do not yet have. Though its origins are ancient, the molecular theory was not generally accepted until about the beginning of the nineteenth century, and even then there were setbacks until experimental evidence vindicated the theory early in the twentieth century. Many pieces of the puzzle of molecular behavior have now fallen into place, but as yet it has not been possible to develop a complete generalization.

In the nineteenth century, the laws of Charles and Gay-Lussac were combined with Avogadro's hypothesis to form the gas law, $PV = NRT,$

which was perhaps the first important correlation of properties. Deviations from the ideal-gas law, though often small, were tied to the fundamental nature of the molecules. The equation of van der Waals, the virial equation, and other equations of state express these quantitatively. These extensions of the ideal-gas law have not only facilitated progress in the development of a molecular theory but, more important for our purposes here, have provided a framework for correlating physical properties of fluids.

The original "hard-sphere" kinetic theory of gases was a significant contribution to progress in understanding the statistical behavior of a system containing a large number of molecules. Thermodynamic and transport properties were related quantitatively to molecular size and speed. Deviations from the hard-sphere kinetic theory led to studies of the interaction of molecules based on the realization that molecules attract at intermediate separations and repel when they come very close. The semiempirical potential functions of Lennard-Jones and others describe attraction and repulsion in an approximate quantitative fashion. More recent potential functions allow for the shapes of molecules and for asymmetric charge distribution in polar molecules.

Although allowance for the forces of attraction and repulsion between molecules is primarily a development of the twentieth century, the concept is not new. In about 1750, Boscovich suggested that molecules (which he referred to as atoms) are "endowed with potential force, that any two atoms attract or repel each other with a force depending on their distance apart. At large distances the attraction varies as the inverse square of the distance. The ultimate force is a repulsion which increases without limit as the distance decreases without limit, so that the two atoms can never coincide" [3].

From the viewpoint of mathematical physics, the development of a comprehensive molecular theory would appear to be complete. J. C. Slater [4] observes that, while we are still seeking the laws of nuclear physics, "in the physics of atoms, molecules and solids, we have found the laws and are exploring the deductions from them." However, the suggestion that, in principle (the Schrödinger equation of quantum mechanics), everything is known about molecules is of little comfort to the engineer who needs to know the properties of some new chemical to design a commercial plant.

Paralleling the continuing refinement of the molecular theory has been the development of thermodynamics and its application to properties. The two are intimately related and interdependent. Carnot was an engineer interested in steam engines, but the second law of thermodynamics was shown by Clausius, Kelvin, Maxwell, and Gibbs to have broad applications in all branches of science.

Thermodynamics by itself cannot provide physical properties; only molecular theory or experiment can do that. But thermodynamics reduces experimental or theoretical efforts by relating one physical property to another. For example, the Clausius-Clapeyron equation provides a useful method for obtaining enthalpies of vaporization from more easily measured vapor pressures.

The second law led to the concept of chemical potential which is basic to an understanding of chemical and phase equilibria, and Maxwell's equations provide ways to obtain important thermodynamic properties of a substance from $PVTx$ relations. Since derivatives are often required, the $PVTx$ function must be known accurately.

In spite of impressive developments in molecular theory, the engineer frequently finds a need for physical properties which have not been measured and which cannot be calculated from existing theory. The *International Critical Tables,* Beilstein, Landolt-Börnstein, and many other handbooks provide convenient data sources, and there exists an increasing number of journals devoted to compilation and critical review of physical property data. Further, computerized data banks are now becoming routine components of computer-aided process design. But it is inconceivable that all desired experimental data will ever be available for the hundreds or thousands of compounds of interest in science and industry: while the number of possibly interesting compounds is already very large, the number of mixtures formed by these compounds is much larger.

While the need for accurate design data is increasing, the rate of accumulation of new data is not increasing fast enough. Data on multicomponent mixtures are particularly scarce. The process engineer who is frequently called upon to design a plant to produce a new chemical (or a well-known chemical in a new way) often finds that the required physical property data are not available. It may be possible to obtain the desired properties from new experimental measurements, but that is often not practical because such measurements tend to be expensive and time-consuming. To meet budgetary and deadline requirements, the process engineer almost always must estimate at least some of the properties required for design.

1-2 Estimation of Properties

In the all-too-frequent situation in which no experimental value of the needed property is at hand, the value must be estimated or predicted. "Estimation" and "prediction" are often used as if they were synonymous, although the former properly carries the frank implication that the result may be only approximate. Estimates may be based on theory, on correlations of experimental values, or on a combination of both. A theoretical

relation, although not generally valid, may nevertheless serve adequately in specific cases.

To relate mass and volumetric flow rates of air through an air-conditioning unit, the engineer is justified in using $PV = NRT$. Similarly, he or she may properly use Dalton's law and the vapor pressure of water to calculate the mass fraction of water in saturated air. However, the engineer must be able to judge the operating pressure when such simple calculations lead to unacceptable error.

Completely empirical correlations are often useful, but one must avoid the temptation to use them outside the narrow range of properties on which they are based. In general, the stronger the theoretical basis, the more reliable the correlation.

Most of the better estimation methods use equations based on the form of an incomplete theory with empirical correlations of the constants that are not provided by that theory. Introduction of empiricism into parts of a theoretical relation provides a powerful method for developing a reliable correlation. For example, the van der Waals equation of state is a modification of the simple $PV = NRT$; setting $N = 1$,

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \tag{1-2.1}$$

Equation (1-2.1) is based on the idea that the pressure on a container wall, exerted by the impinging molecules, is decreased because of the attraction by the mass of molecules in the bulk gas; that attraction rises with density. Further, the available space in which the molecules move is less than the total volume by the excluded volume b due to the size of the molecules themselves. Therefore, the "constants" a and b have some theoretical basis. The correlation of a and b in terms of other properties of a substance is an example of the use of an empirically modified theoretical form.

Empirical extension of theory can often lead to a correlation useful for estimation purposes. For example, several methods for estimating diffusion coefficients in low-pressure binary gas systems are empirical modifications of the equation given by the simple kinetic theory. Almost all the better estimation procedures are based on correlations developed in this way.

1-3 Types of Estimation

An ideal system for the estimation of a physical property would (1) provide reliable physical and thermodynamic properties for pure substances and for mixtures at any temperature, pressure, and composition, (2) indicate the state (solid, liquid, or gas), (3) require a minimum of input data,

(4) choose the least-error route (i.e., the best estimation method), (5) indicate the probable error, and (6) minimize computation time. Few of the available methods approach this ideal, but some serve remarkably well.

In numerous practical cases, the most accurate method may not be the best for the purpose. Many engineering applications properly require only approximate estimates, and a simple estimation method requiring little or no input data is often preferred over a complex but more accurate correlation. The simple gas law is useful at low to modest pressures, although more accurate correlations are available. Unfortunately, it is often not easy to provide guidance on when to reject the simpler in favor of the more complex (but more accurate) method.

Although a variety of molecular theories may be useful for data correlation, there is one theory which is particularly helpful. This theory, called the theory of corresponding states, was originally based on macroscopic arguments, but in its modern form it has a molecular basis.

The law of corresponding states

Proposed by van der Waals in 1873, the law of corresponding states expresses the generalization that equilibrium properties which depend on intermolecular forces are related to the critical properties in a universal way. Corresponding states provides the single most important basis for the development of correlations and estimation methods. In 1873, van der Waals showed it to be theoretically valid for all pure substances whose PVT properties could be expressed by a two-constant equation of state such as Eq. (1-2.1). As shown by Pitzer in 1939, it is similarly valid if the intermolecular potential function requires only two characteristic parameters. Corresponding states holds well for fluids containing simple molecules and, upon semiempirical extension, it also holds for many other substances where molecular orientation is not important, i.e., for molecules that are not strongly polar or hydrogen-bonded.

The relation of pressure to volume at constant temperature is different for different substances; however, corresponding states theory asserts that if pressure, volume, and temperature are related to the corresponding critical properties, the function relating reduced pressure to reduced volume becomes the same for all substances. The reduced property is commonly expressed as a fraction of the critical property: $P_r = P/P_c$; $V_r = V/V_c$; and $T_r = T/T_c$.

To illustrate corresponding states, Fig. 1-1 shows the law of corresponding states for PVT data for methane and nitrogen. In effect, the critical point is taken as the origin. The data for saturated liquid and saturated vapor coincide well for the two substances. The isotherms (constant T_r), of which only one is shown, agree equally well.

Successful application of the law of corresponding states for correlation
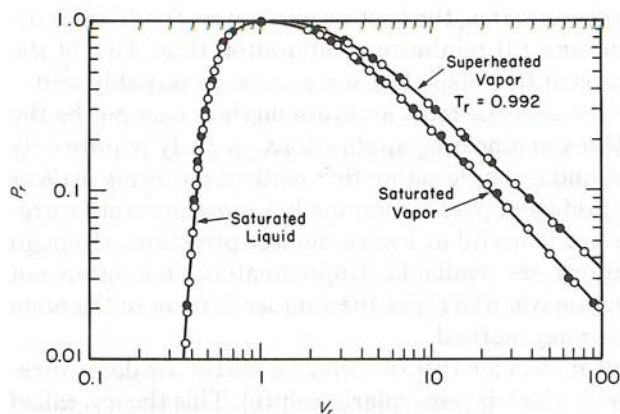
Figure 1-1 The law of corresponding states applied to the PVT properties of methane and nitrogen. Experimental values [2]: o methane, ● nitrogen.

of PVT data has encouraged similar correlations of other properties which depend primarily on intermolecular forces. Many of these have proved valuable to the practicing engineer. Modifications of the law are common to improve accuracy or ease of use. Good correlations of high-pressure gas viscosity have been obtained by expressing η/η_c as a function of P_r and T_r. But since η_c is seldom known and not easily estimated, this quantity has been replaced in other correlations by η_c°, η_T°, or the group $M^{1/2}P_c^{2/3}T_c^{1/6}$, where η_c° is the viscosity at T_c and low pressure, η_T° is the viscosity at the temperature of interest, again at low pressure, and the group containing M, P_c, and T_c is suggested by dimensional analysis. Other alternatives to the use of η_c might be proposed, each modeled on the law of corresponding states but essentially empirical as applied to transport properties.

The law of corresponding states can be derived from statistical mechanics when severe simplifications are introduced into the partition function. Sometimes other useful results can be obtained by introducing less severe simplifications into statistical mechanics toward providing a framework for the development of estimation methods. Fundamental equations describing various properties (including transport properties) can sometimes be derived, provided that an expression is available for the potential-energy function for molecular interactions. This function may be, at least in part, empirical; but the fundamental equations for properties are often insensitive to details in the potential function from which they stem, and two-constant potential functions frequently serve remarkably well for some systems. Statistical mechanics may at present be far removed from engineering practice, but there is good reason to believe that it will become increasingly useful, especially when combined with computer simulations.

Nonpolar and polar molecules

Spherically symmetric molecules (for example, CH_4) are well fitted by a two-constant law of corresponding states. Nonspherical and weakly polar molecules do not fit poorly, but deviations are often great enough to encourage the development of correlations using a third parameter, e.g., the acentric factor. The acentric factor is obtained from the deviation of the experimental vapor pressure–temperature function from that which might be expected for a similar substance consisting of spherically symmetric molecules. Typical corresponding states correlations express the dimensionless property as a function of P_r, T_r, and the chosen third parameter.

Unfortunately, the properties of strongly polar molecules are often not satisfactorily represented by the two- or three-constant correlations which do so well for nonpolar molecules. An additional parameter based on the dipole moment has often been suggested but with limited success, since polar molecules are not easily characterized by using only the dipole moment and critical constants. As a result, although good correlations exist for properties of nonpolar fluids, similar correlations for polar fluids are often not available or else are of restricted reliability.

Structure

All macroscopic properties are related to molecular structure, which determines the magnitude and predominant type of the intermolecular forces. For example, structure determines the energy storage capacity of a molecule and thus the molecule's heat capacity.

The concept of structure suggests that a macroscopic property can be calculated from group contributions. The relevant characteristics of structure are related to the atoms, atomic groups, bond type, etc.; to them we assign weighting factors and then determine the property, usually by an algebraic operation which sums the contributions from the molecule's parts. Sometimes the calculated sum of the contributions is not for the property itself but instead is for a correction to the property as calculated by some simplified theory or empirical rule. For example, Lydersen's method for estimating T_c starts with the loose rule that the ratio of the normal boiling temperature to the critical temperature is about $2:3$. Additive structural increments based on bond types are then used to obtain empirical corrections to that ratio.

Some of the better correlations of ideal-gas heat capacities employ theoretical values of C_p° (which are intimately related to structure) to obtain a polynomial expressing C_p° as a function of temperature; the constants in the polynomial are determined by contributions from the constituent atoms, atomic groups, and types of bonds.

1-4   Organization of the Book

Reliable experimental data are always to be preferred over values obtained by estimation methods. But all too often reliable data are not available.

In this book, the various estimation methods are correlations of experimental data. The best are based on theory, with empirical corrections for the theory's defects. Others, including those stemming from the law of corresponding states, are based on generalizations which are partly empirical but which nevertheless have application to a remarkably wide range of properties. Totally empirical correlations are useful only when applied to situations very similar to those used to establish the correlations.

The text includes a large number of numerical examples to illustrate the estimation methods, especially those which are recommended. Almost all of them are designed to explain the calculation procedure for a single property. However, most engineering design problems require estimation of several properties; the error in each contributes to the overall result, but some individual errors are more important than others. Fortunately, the result is often found adequate for engineering purposes, in spite of the large measure of empiricism incorporated in so many of the estimation procedures.

As an example, consider the case of a chemist who has synthesized a new compound which has the chemical formula CCl_2F_2 and boils at $-20.5°C$ at atmospheric pressure. Using only this information, is it possible to obtain a useful prediction of whether or not the substance has the thermodynamic properties which might make it a practical refrigerant?

Figure 1-2 shows portions of a Mollier diagram developed by the prediction methods described in later chapters. The dashed curves and points are obtained from estimates of liquid and vapor heat capacities, critical properties, vapor pressure, enthalpy of vaporization, and pressure corrections to ideal-gas enthalpies and entropies. The substance is, of course, a well-known refrigerant, and its known properties are shown by the solid curves.

For a standard refrigeration cycle operating between 48.9 and $-6.7°C$, the evaporator and condenser pressures are estimated to be 2.4 and 12.4 bar, vs. the known values 2.4 and 11.9 bar. The estimate of the heat absorption in the evaporator checks closely, and the estimated volumetric vapor rate to the compressor also shows good agreement: 2.39 versus 2.45 m^3/hr per kW of refrigeration. (This number indicates the size of the compressor.) Constant-entropy lines are not shown in Fig. 1-2, but it is found that the constant-entropy line through the point for the low-pressure vapor essentially coincides with the saturated vapor curve. The estimated coefficient of performance (ratio of refrigeration rate to isentropic compression power) is estimated to be 3.8; the value obtained from the
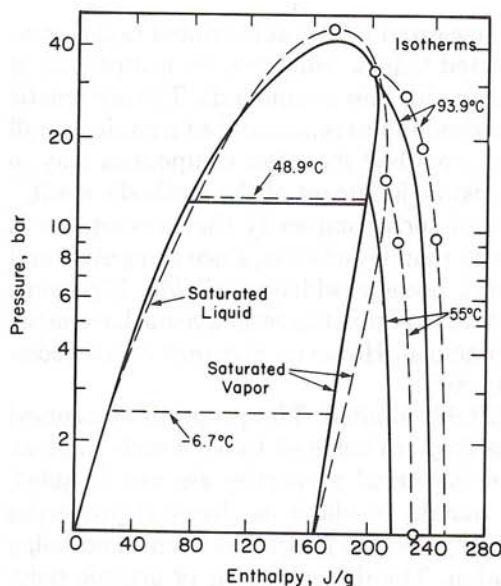
Figure 1-2 Mollier diagram for dichlorodifluoromethane. The solid lines represent measured data. Dashed lines and points represent results obtained by estimation methods when only the chemical formula and the normal boiling temperature are known.

data is 3.5. This is not a very good check, but it is nevertheless remarkable because the only data used for the estimate were the normal boiling point and the chemical formula.

Most estimation methods require parameters which are characteristic of single pure components or of constituents of a mixture of interest. The more important of these are considered in Chap. 2, and tables of values for common substances are provided in Appendix A.

Thermodynamic properties (such as enthalpy and heat capacity) are discussed in Chaps. 3 to 6. Although the more accurate equations of state are employed, the basic thermodynamic relations are developed in a general way so that other equations of state can be introduced whenever they are more applicable for a particular purpose.

Chapters 5 and 6 discuss heat capacities; Chap. 6 discusses Gibbs energy and enthalpy of formation; and Chap. 7 discusses vapor pressures and enthalpies of vaporization of pure substances. Chapter 8 presents techniques for estimation and correlation of phase equilibria in mixtures. Chapters 9 to 11 describe estimation methods for viscosity, thermal conductivity, and diffusion coefficients. Surface tension is considered briefly in Chap. 12.

The literature searched was voluminous, and the lists of references following each chapter represent but a fraction of the material examined. Of the many estimation methods available, only a few were selected for detailed discussion. These were selected on the basis of their generality, accuracy, and availability of required input data. Tests of all methods

were more extensive than those suggested by the abbreviated tables comparing experimental with estimated values. However, no comparison is adequate to indicate expected errors for new compounds. The arithmetic average errors given in the comparison tables represent but a crude overall evaluation; the inapplicability of a method for a few compounds may so increase the average error as to distort judgment of the method's merit.

Many estimation methods are of such complexity that a computer is desirable. This is less of a handicap than it once was, since computers and efficient computer programs have become widely available. Electronic desk computers, which have become so popular in recent years, have made the more complex correlations practical. However, accuracy is not necessarily enhanced by greater complexity.

The scope of the book is inevitably limited. The properties discussed were selected arbitrarily because they are believed to be of wide interest, especially to chemical engineers. Electrical properties are not included, nor are the properties of salts, metals, or alloys or chemical properties other than some thermodynamically derived properties such as enthalpy and the Gibbs energy of formation. The difficult areas of organic polymers and crystals are not included here; introductions are given by Bondi [1] and van Krevelen [5].

This book is intended to provide estimation methods for a limited number of physical properties of fluids. Hopefully, the need for such estimates, and for a book of this kind, may diminish as more experimental values become available and as the continually developing molecular theory advances beyond its present incomplete state. In the meantime, estimation methods are essential for most process design calculations and for many other purposes in engineering and applied science.

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Pure Component Constants

2-1 Scope

Chemical engineers normally deal with mixtures rather than pure materials. However, the chemical compositions of many mixtures are known. Even for poorly characterized mixtures in the petroleum industry, one assigns pseudo pure component constants to fractions of the mixture where the fractions are normally specified by a volatility range. Also, few mixture-property correlations to date have incorporated true mixture parameters. Instead, the techniques employ parameters which are functions only of the properties of the pure components. These *pure component constants* are then used with the state variables such as temperature, pressure, and composition to generate property estimation methods.

In this chapter, we introduce the more common and useful pure component constants and show how they can be estimated if no experimental data are available. A few useful pure component constants, however, are not covered, because it is more convenient and appropriate to discuss them in subsequent chapters. For example, the liquid specific volume (or density) at some reference state (e.g., as a saturated liquid at 1 bar) is a useful pure component constant, yet it is more easily introduced in Chap. 3, where volumetric properties are covered.

The correlations presented in this chapter are primarily of the *group contribution* type. When the molecular structure is not well known, or

when one is interested in, say, characterizing pseudocritical properties of petroleum or coal liquid fractions, other types of estimation methods would then be necessary. For example, Lin and Chao [25] present a technique to estimate critical properties and the acentric factor for quite complex organic compounds (and mixtures) from the average molecular weight, boiling point, and the specific gravity (at 20°C). Similar techniques have also been suggested by others [8, 43, 50].

2-2   Critical properties

Critical temperature, pressure, and volume represent three widely used pure component constants, yet recent experimental measurements are almost nonexistent. In Appendix A we have tabulated the critical properties of many materials. In most cases the values given were measured. An excellent compilation of critical properties is available in a National Physical Laboratory Report [4] by Ambrose. Earlier reviews were given by Kudchadker et al. [22] for organic compounds and Mathews [27] for inorganic compounds. The Design Institute for Physical Property Data [10] also presents a detailed discussion of critical properties and their estimation.

Estimation techniques

Ambrose method [2, 3].   In this method, the three critical properties T_c, P_c, and V_c are estimated by a group contribution technique using the following relations:

$$T_c = T_b[1 + (1.242 + \Sigma\Delta_T)^{-1}] \tag{2-2.1}$$

$$P_c = M(0.339 + \Sigma\Delta_P)^{-2} \tag{2-2.2}$$

$$V_c = 40 + \Sigma\Delta_V \tag{2-2.3}$$

The units employed are kelvins, bars, and cubic centimeters per mole.†
For perfluorinated compounds or for compounds containing only halogens (including fluorine), the constant 1.242 in Eq. (2-2.1) would be replaced by 1.570 and the constant 0.339 in Eq. (2-2.2) by 1.000. The Δ quantities are evaluated by summing contributions for various atoms or groups of atoms as shown in Table 2-1. To employ these relations, the normal boiling point T_b (at 1 atm) and the molecular weight M are needed. The technique is illustrated in Example 2-1, and the expected errors are noted later after alternate methods are introduced.

Joback modification of Lydersen's method.   One of the first very successful group contribution methods to estimate critical properties was developed

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†Only the gram mole is used in this book.

TABLE 2-1   Ambrose Group Contributions for Critical Constants

	T_c	P_c	V_c
		Δ values for	
Carbon atoms in alkyl groups	0.138	0.226	55.1
Corrections:			
>CH− (each)	−0.043	−0.006	−8
>C< (each)	−0.120	−0.030	−17
Double bonds (nonaromatic)	−0.050	−0.065	−20
Triple bonds	−0.200	−0.170	−40
Delta Platt number,[1] multiply by	−0.023	−0.026	—
Aliphatic functional groups:			
−O−	0.138	0.160	20
>CO	0.220	0.282	60
−CHO	0.220	0.220	55
−COOH	0.578	0.450	80
−CO−O−OC−	1.156	0.900	160
−CO−O−	0.330	0.470	80
−NO₂	0.370	0.420	78
−NH₂	0.208	0.095	30
−NH−	0.208	0.135	30
>N−	0.088	0.170	30
−CN	0.423	0.360	80
−S−	0.105	0.270	55
−SH	0.090	0.270	55
−SiH₃	0.200	0.460	119
−O−Si(CH₃)₂	0.496	—	—
−F	0.055	0.223	14
−Cl	0.055	0.318	45
−Br	0.055	0.500	67
−I	0.055	—	90
Halogen correction in aliphatic compounds:			
F is present	0.125	—	—
F is absent, but Cl, Br, I are present	0.055	—	—
Aliphatic alcohols[2]	[3]	[4]	15
Ring compound increments (listed only when different from aliphatic values):			
−CH₂−, >CH−, >C<	0.090	0.182	44.5
>CH− in fused ring	0.030	0.182	44.5
Double bond	−0.030	—	−15
−O−	0.090	—	10
−NH−	0.090	—	—
−S−	0.090	—	30
Aromatic compounds:			
Benzene	0.448	0.924	[5]
Pyridine	0.448	0.850	
C₄H₄ (fused as in naphthalene)	0.220	0.515	
−F	0.080	0.183	
−Cl	0.080	0.318	
−Br	0.080	0.600	
−I	0.080	0.850	
−OH	0.198	−0.025	
Corrections for nonhalogenated substitutions:			
First	0.010	0	
Each subsequent	0.030	0.020	
Ortho pairs containing −OH	−0.080	−0.050	
Ortho pairs with no −OH	−0.040	−0.050	

TABLE 2-1   Ambrose Group Contributions for Critical Constants (*Continued*)

	Δ values for		
	T_c	P_c	V_c
Highly fluorinated aliphatic compounds:			
$-CF_3$, $-CF_2-$, $>CF-$	0.200	0.550	
$-CF_2$, $>CF-$ (ring)	0.140	0.420	
$>CF-$ (in fused ring)	0.030	—	
$-H$ (monosubstitution)	-0.050	-0.350	
Double bond (nonring)	-0.150	-0.500	
Double bond (ring)	-0.030	—	
(Other increments as in nonfluorinated compounds)			

[1]The delta Platt number is defined as the Platt number of the isomer minus the Platt number of the corresponding alkane. (For *n*-alkanes, the Platt number is $n - 3$.) The Platt number is the total number of groups of four carbon atoms three bonds apart [40, 41]. This correction is used only for branched alkanes.

[2]Includes naphthenic alcohols and glycols but not aromatic alcohols such as xylenol.

[3]First determine the hydrocarbon homomorph, i.e., substitute $-CH_3$ for each $-OH$ and calculate $\Sigma\Delta_T$ for this compound. Subtract 0.138 from $\Sigma\Delta_T$ for each $-OH$ substituted. Next, add $0.87 - 0.11n + 0.003n^2$ where $n = [T_b$ (alcohol, K) $- 314]/19.2$. Exceptions include methanol ($\Sigma\Delta_T = 0$), ethanol ($\Sigma\Delta_T = 0.939$), and any alcohol whose value of *n* exceeds 10.

[4]Determine the hydrocarbon homomorph as in footnote 3. Calculate $\Sigma\Delta_P$ and subtract 0.226 for each $-OH$ substituted. Add $0.100 - 0.013n$, where *n* is computed as in footnote 3.

[5]When estimating the critical volumes of aromatic substances, use ring compound values, if available, and correct for double bonds.

by Lydersen [26] in 1955. Since that time, more experimental values have been reported and efficient statistical techniques have been developed to determine the optimum group contributions. Joback [19] reevaluated Lydersen's scheme, added several functional groups, and determined the values of the group contributions. His proposed relations are

$$T_c = T_b[0.584 + 0.965\Sigma\Delta_T - (\Sigma\Delta_T)^2]^{-1} \tag{2-2.4}$$

$$P_c = (0.113 + 0.0032n_A - \Sigma\Delta_P)^{-2} \tag{2-2.5}$$

$$V_c = 17.5 + \Sigma\Delta_V \tag{2-2.6}$$

As with the Ambrose method, the units are kelvins, bars, and cubic centimeters per mole. n_A is the number of atoms in the molecule. The Δ values are given in Table 2-2, and the procedure is illustrated in Example 2-2.

Fedors method [13].   The Fedors group contribution method is valid only for critical temperatures. As will be seen later, it is less accurate than the methods of Ambrose and Joback, but it has the advantage of not requiring the normal boiling point to calculate T_c. The Fedors equation may be written as

$$T_c = 535 \log \Sigma\Delta_T \tag{2-2.7}$$

TABLE 2-2   Joback Group Contributions for Critical Properties, the Normal Boiling Point, and the Freezing Point

	T_c	P_c	Δ V_c	T_b	T_f
Nonring increments:					
$-CH_3$	0.0141	−0.0012	65	23.58	−5.10
$>CH_2$	0.0189	0	56	22.88	11.27
$>CH-$	0.0164	0.0020	41	21.74	12.64
$>C<$	0.0067	0.0043	27	18.25	46.43
$=CH_2$	0.0113	−0.0028	56	18.18	−4.32
$=CH-$	0.0129	−0.0006	46	24.96	8.73
$=C<$	0.0117	0.0011	38	24.14	11.14
$=C=$	0.0026	0.0028	36	26.15	17.78
$\equiv CH$	0.0027	−0.0008	46	9.20	−11.18
$\equiv C-$	0.0020	0.0016	37	27.38	64.32
Ring increments:					
$-CH_2-$	0.0100	0.0025	48	27.15	7.75
$>CH-$	0.0122	0.0004	38	21.78	19.88
$>C<$	0.0042	0.0061	27	21.32	60.15
$=CH-$	0.0082	0.0011	41	26.73	8.13
$=C<$	0.0143	0.0008	32	31.01	37.02
Halogen increments:					
$-F$	0.0111	−0.0057	27	−0.03	−15.78
$-Cl$	0.0105	−0.0049	58	38.13	13.55
$-Br$	0.0133	0.0057	71	66.86	43.43
$-I$	0.0068	−0.0034	97	93.84	41.69
Oxygen increments:					
$-OH$ (alcohol)	0.0741	0.0112	28	92.88	44.45
$-OH$ (phenol)	0.0240	0.0184	−25	76.34	82.83
$-O-$ (nonring)	0.0168	0.0015	18	22.42	22.23
$-O-$ (ring)	0.0098	0.0048	13	31.22	23.05
$>C=O$ (nonring)	0.0380	0.0031	62	76.75	61.20
$>C=O$ (ring)	0.0284	0.0028	55	94.97	75.97
$O=CH-$ (aldehyde)	0.0379	0.0030	82	72.24	36.90
$-COOH$ (acid)	0.0791	0.0077	89	169.09	155.50
$-COO-$ (ester)	0.0481	0.0005	82	81.10	53.60
$=O$ (except as above)	0.0143	0.0101	36	−10.50	2.08
Nitrogen increments:					
$-NH_2$	0.0243	0.0109	38	73.23	66.89
$>NH$ (nonring)	0.0295	0.0077	35	50.17	52.66
$>NH$ (ring)	0.0130	0.0114	29	52.82	101.51
$>N-$ (nonring)	0.0169	0.0074	9	11.74	48.84
$-N=$ (nonring)	0.0255	−0.0099	—	74.60	—
$-N=$ (ring)	0.0085	0.0076	34	57.55	68.40
$-CN$	0.0496	−0.0101	91	125.66	59.89
$-NO_2$	0.0437	0.0064	91	152.54	127.24
Sulfur increments:					
$-SH$	0.0031	0.0084	63	63.56	20.09
$-S-$ (nonring)	0.0119	0.0049	54	68.78	34.40
$-S-$ (ring)	0.0019	0.0051	38	52.10	79.93

TABLE 2-3   Fedors Group Contributions for Critical Temperature

Group	Δ_T	Group	Δ_T
$-CH_3$	1.79	$-NH-$ (aromatic)	7.64
$-CH_2-$	1.34	$>N-$	0.89
$>CH-$†	0.45	$>N-$ (aromatic)	4.74
$>C<$	−0.22	$-N=$	4.51
$=CH_2$	1.59	$-S-S-$	9.83
$=CH-$	1.40	$-S-$	4.91
$>C=$	0.89	$-SH$	5.36
$\equiv CH$	1.79	$-F$	2.10
$\equiv C-$	2.46	$-F$ (aromatic)	0.45
$=C=$	1.03	$-F$ (perfluoro)	0.54
$-COOH$	10.72	$-Cl$	4.20
$-CO-O-OC-$ (anhydride)	7.95	$-Cl$ (disubstituted)	3.71
$-CO-O-$	5.32	$-Cl$ (trisubstituted)	3.17
$-O-OC-CO-O-$ (oxalate)	6.25	$-Br$	5.58
$-CO-$	5.36	$-I$	8.04
$-O-$	1.56	$-I$ (aromatic)	10.77
$-O-$ (aromatic)	2.68	Three-membered ring	0.45
$-OH$	5.63	Five-membered ring	2.23
$-OH$ (aromatic)	9.65	Six-membered ring	2.68
$-CHO$	5.49	Heteroatom in ring	0.45
$-C\equiv N$	8.49	Substitution on carbon in a double	
$-C\equiv N$ (aromatic)	9.38	bond (nonaromatic)	0.58
$-NH_2$	4.56	Orthosubstitution in a benzene	
$-NH_2$ (aromatic)	9.20	ring	1.16
$-NH-$	3.04	Conjugation, per double bond	0.13

†Except for adjacent pairs of $>CH-$; then add 0.76 for each.

with T_c in kelvins. The Δ values are shown in Table 2-3, and the method is illustrated in Example 2-3.

Example 2-1   Since the Ambrose method is somewhat more complicated than other methods, this example treats several types of compounds to illustrate some of the less obvious features.
Estimate the critical properties of the following compounds; for most, the experimental critical values shown are from Appendix A (when available) as well as the values of T_b and M necessary to use Ambrose's method.

Compound	T_b, K	M	T_c, K	P_c, bar	V_c, cm³/mol
(a) 2,2,3-Trimethylpentane	383.0	114.23	563.5	27.3	436
(b) 1,trans-3,5-Trimethylcyclohexane	413.7	126.24	602.2	—	—
(c) 1,2,3-Trimethylbenzene	449.3	120.20	664.5	34.5	430
(d) 3-Methylbutan-2-one	367.5	86.13	553.4	38.5	310
(e) N-Methylaniline	469.4	107.16	701	52.0	—
(f) 2-Methylpentan-2-ol	394.2	102.18	559.5	—	—
(g) 1,2,3,4-Tetrafluorobenzene	367.5	150.08	550.8	37.9	313
(h) 1-Chloro-2,2-difluoroethylene	254.6	98.48	400.6	44.6	197
(i) Perfluorocyclohexene	325.2	262.06	461.8	—	—

solution

(a) 2,2,3-TRIMETHYLPENTANE. There are eight aliphatic carbons, one $>$CH$-$ and one $>$C$<$. To obtain the delta Platt number, the Platt number for the isomer and alkane (n-octane) are:

$$
\begin{array}{cc}
C_6 & C_8 \\
| & | \\
C_1-C_2-C_3-C_4-C_5 & \qquad C_1-C_2-C_3-C_4-C_5-C_6-C_7-C_8 \\
| & \\
C_7 &
\end{array}
$$
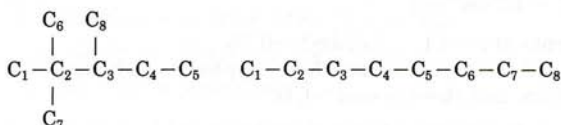
The carbon groups three bonds apart are:
For 2,2,3-trimethylpentane: 1-4, 2-5, 4-6, 4-7, 1-8, 6-8, 7-8, and 5-8, and the Platt number is 8.
For n-octane: 1-4, 2-5, 3-6, 4-7, and 5-8, and the Platt number is 5.
The delta Platt number $= 8 - 5 = 3$.

$$\Sigma\Delta_T = (8)\,(0.138) - 0.043 - 0.120 + (3)\,(-0.023) = 0.872$$

$$\Sigma\Delta_P = (8)\,(0.226) - 0.006 - 0.030 + (3)\,(-0.026) = 1.694$$

$$\Sigma\Delta_V = (8)\,(55.1) - 8 - 17 = 416$$

With Eqs. (2-2.1) to (2-2.3)

$$T_c = (383.0)\,[1 + (1.242 + 0.872)^{-1}] = 564.2 \text{ K}$$

$$P_c = (114.23)\,(0.339 + 1.694)^{-2} = 27.6 \text{ bar}$$

$$V_c = 40 + 416 = 456 \text{ cm}^3/\text{mol}$$

The percent errors in T_c, P_c, and V_c are 0.1, 1.1, and 4.6%.

(b) 1,*trans*-3,5-TRIMETHYLCYLOHEXANE. There are nine carbon atoms. Three are alkyl $-$CH$_3$, three are ring $-$CH$_2-$, and three are ring $>$CH. No delta Platt number is involved.

$$\Sigma\Delta_T = (6)\,(0.138) + (3)\,(0.090) + (3)\,(-0.043) = 0.969$$

$$\Sigma\Delta_P = (6)\,(0.226) + (3)\,(0.182) + (3)\,(-0.006) = 1.884$$

$$\Sigma\Delta_V = (3)\,(55.1) + (3)\,(44.5) + (3)\,(44.5) = 432$$

With Eqs. (2-2.1) to (2-2.3)

$$T_c = (413.7)\,[1 + (1.242 + 0.969)^{-1}] = 600.8 \text{ K}$$

$$P_c = (126.24)\,(0.339 + 1.884)^{-2} = 25.5 \text{ bar}$$

$$V_c = 40 + 432 = 472 \text{ cm}^3/\text{mol}$$

The percent error for T_c is 0%. No experimental values exist for P_c and V_c. The fact that the configuration is trans does not enter into the calculations.

(c) 1,2,3-TRIMETHYLBENZENE. This is an aromatic compound. For T_c and P_c there are three alkyl $-$CH$_3$, one benzene group, and corrections for ring substitutions and the presence of ortho groups. For V_c, there are three alkyl $-$CH$_3$, three $>$CH$-$, three $>$C$<$, and three double bonds.

$$\Sigma\Delta_T = 0.448 + (3)\,(0.138) + 0.010 + (2)\,(0.030) + (2)\,(-0.040) = 0.852$$

$$\Sigma\Delta_P = (0.924) + (3)\,(0.226) + 0 + (2)\,(0.020) + (2)\,(-0.050) = 1.542$$

$$\Sigma\Delta_V = (3)\,(55.1) + (3)\,(44.5) + (3)\,(44.5) + (3)\,(-15) = 387$$

With Eqs. (2-2.1) to (2-2.3)

$$T_c = (449.3) \, [1 + (1.242 + 0.852)^{-1}] = 663.9 \text{ K}$$
$$P_c = (120.20) \, (0.339 + 1.542)^{-2} = 34.0 \text{ bar}$$
$$V_c = 40 + 387 = 427 \text{ cm}^3/\text{mol}$$

The percent errors are −0.1, −1.5, and −0.7%.

(d) 3-METHYLBUTAN-2-ONE. There are four aliphatic carbons; there is one >CH− correction; and there is one >CO.

$$\Sigma\Delta_T = (4) \, (0.138) - 0.043 + 0.220 = 0.729$$
$$\Sigma\Delta_P = (4) \, (0.226) - 0.006 + 0.282 = 1.180$$
$$\Sigma\Delta_V = (4) \, (55.1) - 8 + 60 = 272$$

Then,

$$T_c = (367.5) \, [1 + (1.242 + 0.729)^{-1}] = 554.0 \text{ K}$$
$$P_c = (86.13) \, (0.339 + 1.180)^{-2} = 37.3 \text{ bar}$$
$$V_c = 40 + 272 = 312 \text{ cm}^3/\text{mol}$$

The percent errors are 0.1, −3.1, and 0.6%.

(e) N-METHYLANILINE. For T_c and P_c, there is a benzene ring, one alkyl −CH_3, one aliphatic >NH, and a correction for aromatic substitution. For V_c, there is one alkyl CH_3−, one aliphatic >NH, five ring >CH−, one ring >C<, and three double bonds.

$$\Sigma\Delta_T = 0.448 + 0.138 + 0.01 + 0.208 = 0.804$$
$$\Sigma\Delta_P = 0.924 + 0.226 + 0.135 = 1.285$$
$$\Sigma\Delta_V = 55.1 + 30 + (5) \, (44.5) + 44.5 + (3) \, (-15) = 307$$

With Eqs. (2-2.1) to (2-2.3)

$$T_c = (469.4) \, [1 + (1.242 + 0.804)^{-1}] = 699 \text{ K}$$
$$P_c = (107.16) \, (0.339 + 1.285)^{-2} = 40.6 \text{ bar}$$
$$V_c = 40 + 307 = 347 \text{ cm}^3/\text{mol}$$

The percent errors in T_c and P_c are −0.3 and −22%. The estimate for critical pressure in this case is quite poor, and it seems probable that the experimental value is in error.

(f) 2-METHYLPENTAN-2-OL. The hydrocarbon homomorph of 2-methylpentan-2-ol is 2,2-dimethylpentane, and we need to determine $\Sigma\Delta_T$ and $\Sigma\Delta_P$ for the latter.

$$\Sigma\Delta_T = (7) \, (0.138) - 0.120 = 0.846$$
$$\Sigma\Delta_P = (7) \, (0.226) - 0.030 = 1.552$$

For the critical temperature we need to correct $\Sigma\Delta_T$ as indicated in the footnotes of Table 2-1, i.e., subtract 0.138 for the −OH. Also, we calculate

$$n = \frac{T_b \, (\text{alcohol}) - 314.1}{19.2} = \frac{394.2 - 314.1}{19.2} = 4.17$$

and determine the correction = $(0.87 - 0.11n + 0.003n^2) = 0.463$. Then,

$$\Sigma\Delta_T \, (\text{alcohol}) = 0.846 - 0.138 + 0.463 = 1.171$$

In a similar manner, for $\Sigma\Delta_P$, with $n = 4.17$

$$\Sigma\Delta_P \, (\text{alcohol}) = 1.552 - 0.226 + [0.100 - (0.013) \, (4.17)] = 1.372$$

For $\Sigma\Delta_V$, we do not require these corrections, so

$\Sigma\Delta_V = (6)\,(55.1) - 17 + 15 = 329 \text{ cm}^3/\text{mol}$

Then we can use Eqs. (2-2.1) to (2-2.3)

$T_c = (394.2)\,[1 + (1.242 + 1.171)^{-1}] = 557.6 \text{ K}$

$P_c = (102.18)\,(0.339 + 1.372)^{-2} = 34.9 \text{ bar}$

$V_c = 40 + 329 = 369 \text{ cm}^3/\text{mol}$

Only the critical temperature is known; for this property, the percent error is -0.3%

(g) 1,2,3,4-TETRAFLUOROBENZENE. Since tetrafluorobenzene is not a fluorinated aliphatic compound, the estimation method uses the benzene ring plus four aromatic $-F$ contributions for T_c and P_c. For V_c, we have two ring $>CH-$, four ring $>C<$, three double bonds, and, since no aromatic values are available, four aliphatic $-F$.

$\Sigma\Delta_T = 0.448 + (4)\,(0.080) = 0.768$

$\Sigma\Delta_P = 0.924 + (4)\,(0.183) = 1.656$

$\Sigma\Delta_V = (2)\,(44.5) + (4)\,(44.5) + (3)\,(-15) + (4)\,(14) = 278$

$T_c = (367.5)\,[1 + (1.242 + 0.768)^{-1}] = 550.3 \text{ K}$

$P_c = (150.08)\,(0.339 + 1.656)^{-2} = 37.7 \text{ bar}$

$V_c = 40 + 278 = 318 \text{ cm}^3/\text{mol}$

The percent errors are -0.1, -0.5, and 1.6%.

(h) 1-CHLORO-2,2-DIFLUOROETHYLENE. Here we have two aliphatic carbons, a double bond, a fluorine correction, two $-F$, and one $-Cl$.

$\Sigma\Delta_T = (2)\,(0.138) - 0.050 + 0.125 + (2)\,(0.055) + 0.055 = 0.5l6$

$\Sigma\Delta_P = (2)\,(0.226) - 0.065 + (2)\,(0.223) + 0.318 = 1.151$

$\Sigma\Delta_V = (2)\,(55.1) - 20 + (2)\,(14) + 45 = 163$

$T_c = (254.6)\,[1 + (1.242 + 0.516)^{-1}] = 399.4 \text{ K}$

$P_c = (98.48)\,(0.339 + 1.151)^{-2} = 44.4 \text{ bar}$

$V_c = 40 + 163 = 203 \text{ cm}^3/\text{mol}$

The percent errors are -0.3, -0.4, and 3.0%.

(i) PERFLUOROCYCLOHEXENE. In this final case, we have a perfluorinated compound, so that constants 1.242 and 0.339 in Eqs. (2-2.1) and (2-2.2) are changed to 1.570 and 1.00. We have four $(-CF_2)_{\text{ring}}$, two $(>CF-)_{\text{ring}}$, and one ring double bond. For V_c, we describe the structure with six ring $>C<$, one double bond, and ten aliphatic $-F$.

$\Sigma\Delta_T = (4)\,(0.140) + (2)\,(0.140) - 0.030 = 0.810$

$\Sigma\Delta_P = (4)\,(0.420) + (2)\,(0.420) - 0 = 2.520$

$\Sigma\Delta_V = (6)\,(44.5) - 15 + (10)\,(14) = 392$

$T_c = (325.2)\,[1 + (1.570 + 0.810)^{-1}] = 461.9 \text{ K}$

$P_c = (262.06)\,(1.00 + 2.52)^{-2} = 21.1 \text{ bar}$

$V_c = 40 + 392 = 432 \text{ cm}^3/\text{mol}$

Only T_c is known; the error is 0.1%.

Example 2-2 Using the Joback modification of Lydersen's method, estimate the critical properties of 3-methylbutan-2-one.

solution   With Table 2-2, for this compound

	Δ_T	Δ_P	Δ_V
(3) $-CH_3$	(3) (0.0141)	(3) (−0.0012)	(3) (65)
$>CH-$	0.0164	0.0020	41
$C=0$	0.0380	0.0031	62
	0.0967	0.0015	298

Thus $\Sigma\Delta_T = 0.0976$, $\Sigma\Delta_P = 0.0015$, $\Sigma\Delta_V = 298$, and the number of atoms n_A is equal to 16 ($C_5H_{10}O$). With Eqs. (2-2.4) to (2-2.6) and with $T_b = 367.5$ K from the table in Example 2-1,

$T_c = (367.5) [0.584 + (0.965) (0.0967) - (0.0967)^2]^{-1} = 550.2$ K

$P_c = [0.113 + (0.0032) (16) - 0.0015]^{-2} = 37.8$ bar

$V_c = 17.5 + 298 = 315.5$ cm³/mol

The percent errors are -0.6, 1.9, and 1.7% for T_c, P_c, and V_c. Shown below are the percent errors found for Joback's technique with the other compounds tested in Example 2-1.

	Percent error in				Percent error in		
Compound	T_c	P_c	V_c	Compound	T_c	P_c	V_c
(a)	0.4	−4.4	7.0	(f)	−1.2	—	—
(b)	1.4	—	—	(g)	3.6	−7.4	7.0
(c)	−0.3	−8.6	0.3	(h)	−0.1	2.4	8.3
(d)	−0.6	1.9	1.7	(i)	−2.3	—	—
(e)	0	−20	—				

Example 2-3   Using Fedors method, estimate the critical temperature of 2,2,3-trimethylpentane.

solution   Using Table 2-3,

$\Sigma\Delta_T = (5) (-CH_3) + -CH_2 + >CH- + >C< = (5) (1.79) + 1.34 + 0.45 - 0.22$

$= 10.52$

With Eq. (2-2.7),

$T_c = (535) (\log_{10} 10.52) = 546.8$ K

The percent error is -3.0%. For the various compounds tested in Example 2-1, the Fedors method was found to give percent errors of (a) -3.0%, (b) 0.2%, (c) -0.4%, (d) 1.3%, (e) -0.7%, (f) 8.0%, (g) 12%, (h) 46%, and (i) 17%.

Discussion

For *critical temperatures,* a comparison was made between experimental values and the values estimated by the methods of Ambrose and Joback.

Over 400 compounds from Appendix A were included. The results are shown below.

	Ambrose	Joback
Mean of the absolute error, K	4.3	4.8
Average of the absolute percent error	0.7	0.8

The Ambrose method yields the smaller error, but it is somewhat more complicated in its use than Joback's. Other recent group contribution estimation methods were also evaluated [14, 18, 21, 47]. The Fishtine procedure [14] shows errors comparable to those found above, but it involves a reference substance of "similar" structure whose properties must be known. The other references cited showed higher errors in the testing than either the method of Ambrose or that of Joback, or they were limited to hydrocarbons.

The Design Institute for Physical Property Data [10] recommends either Fishtine's or Ambrose's method for nonhydrocarbons and the API technique for hydrocarbons [6].

We suggest either the Ambrose or the Joback form to estimate T_c when a reliable value of T_b is known. The Fedors relation, Eq. (2-2.7), is of value when T_b is not known. For many compounds, it yields a relatively small error, but for some materials (see Example 2-3), the accuracy is poor.

Finally, we note a deceptively simple relation derived by Klincewicz [20, 21] which involves no group contributions.

$$T_c = 50.2 - 0.16M + 1.41T_b \qquad (2\text{-}2.8)$$

where T_b is the normal boiling temperature (at 1 atm) in kelvins and M is the molecular weight. When Eq. (2-2.8) was used to estimate T_c for the compounds in Example 2-1, the percent errors were (a) 1.5%, (b) 1.8%, (c) 0%, (d) 0.2%, (e) −0.9%, (f) 5.4%, (g) −1.2%, (h) −1.8%, and (i) 1.1%. Except for case (f), the errors found range from about 1 to 2 percent. This is typical of the range found in more extensive testing.

For *critical pressure*, all the estimation methods tested yielded higher percent errors than for critical temperature, and the database employed was somewhat smaller. About 390 compounds were tested. The results for the Ambrose and Joback methods are shown below.

	Ambrose	Joback
Mean of the absolute error, bar	1.8	2.1
Average of the absolute percent error	4.6	5.2

These errors are typical of those shown in Examples 2-1 and 2-2. The very large error for N-methylaniline is suspect. The experimental value for this material was listed by Kudchadker et al. [22].

A number of other estimation methods also were examined [14, 20, 21, 26, 34, 44, 47]. The Fishtine procedure [14] is similar in accuracy to the methods of Ambrose and Joback but, as noted earlier in the discussion on critical temperature, it requires the choice of a reference material of similar structure. It was tested, along with Ambrose's, by Danner and Daubert [10] and found to be about equal in accuracy for nonhydrocarbons. For hydrocarbons, these authors recommend the method in [6].

We recommend the method of either Ambrose or Joback to estimate critical pressures. In the former the molecular weight is employed as a secondary parameter, whereas in the latter, the number of atoms is used instead.

For *critical volume,* the Ambrose and Joback methods were tested with data from 310 compounds. The associated errors were found to be

	Ambrose	Joback
Mean of the absolute error, cm³/mol	8.5	7.5
Average of the absolute percent error	2.8	2.3

Several other recent estimation methods for critical volume also were evaluated. The methods of Fishtine [14], Vetere [48], Fedors [11, 12], and Klincewicz [20, 21] are also group contribution methods. They are not recommended relative to the Ambrose or the Joback technique either because the overall accuracy was less or because they could not treat as wide a range of compounds. Nath [33] has also proposed that V_c be estimated from T_c, P_c, and the acentric factor, but the correlation is limited to nonpolar substances.

We recommend either the Joback or the Ambrose method to estimate critical volumes. Expected errors are in the range of 5 to 10 percent. Danner and Daubert [10], however, recommend the Fedors method [12].

As a final comment relative to the estimation of critical properties, we note that occasionally one may "back out" critical properties from experimental data if a corresponding states correlation is believed to be applicable. That is, if the property were some function of reduced temperature (T/T_c), reduced pressure (P/P_c), and/or reduced volume (V/V_c), then by knowing the values of the property over a range of temperatures, pressures, and/or volumes, it is possible to estimate "characteristic" critical properties. See, for example, Refs. 5, 15, and 24.

2-3 Acentric Factor

One of the more common pure component constants is the acentric factor [38, 39], which is defined as

$$\omega = -\log P_{vp_r} \text{ (at } T_r = 0.7) - 1.000 \tag{2-3.1}$$

To obtain values of ω, the reduced vapor pressure ($P_r = P/P_c$) at $T_r = T/T_c = 0.7$ is required.

As originally proposed, ω represented the acentricity or nonsphericity of a molecule. For monatomic gases, ω is, therefore, essentially zero. For methane, it is still very small. However, for higher-molecular-weight hydrocarbons, ω increases. It also rises with polarity. At present, ω is very widely used as a parameter which in some manner is supposed to measure the complexity of a molecule with respect to both the geometry and polarity, but the large values of ω for some polar compounds ($\omega > 0.4$) are not meaningful in the context of the original meaning of this property.

We show in Appendix A the acentric factor for many materials. The values were obtained, in most cases, from experimental data on T_c, P_c, and vapor pressures.

If acentric factors are needed for a material not shown in Appendix A, the usual technique is to locate (or estimate) the critical constants T_c and P_c and then determine the vapor pressure at $T_r = 0.7$. This latter estimation would normally be made by using one of the reduced vapor pressure correlations given later in Chap. 7. As an example, if the vapor pressure correlation chosen were

$$\log P_{vp} = A + \frac{B}{T} \tag{2-3.2}$$

with A and B found, say, from the sets (T_c, P_c; T_b, $P = 1$ atm), then

$$\omega = \frac{3}{7} \frac{\theta}{1 - \theta} \log P_c - 1 \tag{2-3.3}$$

where P_c, in this case, must be expressed in atmospheres and $\theta = T_b/T_c$.

Similarly, if the Lee-Kesler vapor pressure relations (7-2.6) to (7-2.8) were used,

$$\omega = \frac{\alpha}{\beta} \tag{2-3.4}$$

where $\alpha = -\ln P_c - 5.92714 + 6.09648\theta^{-1} + 1.28862 \ln \theta - 0.169347\theta^6$
          $\beta = 15.2518 - 15.6875\theta^{-1} - 13.4721 \ln \theta + 0.43577\theta^6$

and P_c is in atmospheres. Lee and Kesler [23] report that Eq. (2-3.4) yields values of ω very close to those selected by Passut and Danner [36] and Henry and Danner [16] in their critical reviews.

Example 2-4 Estimate the acentric factor of isopropylbenzene by using Eqs. (2-3.3) and (2-3.4). The accepted value is 0.326.

solution From Appendix A, $T_c = 631.1$ K, $T_b = 425.6$ K, $P_c = 32.1$ bar $= 31.7$ atm. Thus, $\Theta = (425.6/631.1) = 0.674$. With Eq. (2-3.3),

$$\omega = \frac{3}{7}\frac{0.674}{1 - 0.674}\log 31.7 - 1$$

$$= 0.330$$

Using Eq. (2-3.4),

$$\alpha = -\ln(31.7) - 5.92714 + (6.09648)(0.674)^{-1} + (1.28862)\ln(0.674)$$
$$- (0.169347)(0.674)^6$$
$$= -0.8669$$

$$\beta = 15.2518 - (15.6875)(0.674)^{-1} - (13.4721)\ln(0.674) + (0.43577)(0.674)^6$$
$$= -2.662$$

$$\omega = \frac{\alpha}{\beta} = \frac{-0.8669}{-2.662} = 0.326$$

In many instances in the literature, one finds ω related to Z_c by

$$Z_c = \frac{P_c V_c}{RT_c} = 0.291 - 0.080\omega \tag{2-3.5}$$

This equation results from applying a PVT correlation that employs ω at the critical point, where $Z = Z_c$. Equation (2-3.5) is only very approximate, as the reader can readily show from the values in Appendix A.

In other recent papers dealing with the acentric factor, Nath [32] relates ω to the enthalpy of vaporization and to the reduced temperature; Hoshino et al. [17] propose a group contribution method to estimate ω that is applicable to saturated hydrocarbons.

Chappelear [9] makes an observation that, over the years, the "accepted" values of the acentric factor may change due to new vapor pressure data or critical constants. However, if one is using a correlation that was developed from earlier values of ω, then these acentric factors should be employed and not the newer, updated values. She notes the problem of carbon dioxide in particular. In Appendix A, we show $\omega = 0.225$; others have quoted a value of 0.267 [35]. The differences result from the extrapolation technique used to extend the liquid region past the freezing point to a reduced temperature of 0.7. Neither $\omega = 0.225$ nor $\omega = 0.267$ can be considered a firm value, but if one were to use a correlation such as the Peng-Robinson equation of state [37], the acentric factor value of CO_2 should be 0.225, since that was the value used by Peng and Robinson to develop their correlation.

2-4   Boiling and Freezing Points

Ordinarily, when one refers to a freezing or boiling point, there is an implied condition that the pressure is 1 atm. A more exact terminology for these temperatures might be the *normal freezing* and *boiling points*. In Appendix A, values for T_f and T_b are given for many substances.

A number of methods to estimate the normal boiling point have been proposed. Many are reviewed in a previous edition of this book [42]. More recent techniques are usually specific for a given homologous series as, for example, the work of Ambrose [1] on alkanols. Others, e.g., [30, 31], attempt to use London's theory to relate T_b to basic molecular parameters such as ionization potential, molar refraction, and shape. None in this latter class yield accurate estimations, but they can provide useful guidelines.

To obtain a very approximate guess of T_b, one may use the group contributions for T_b in Table 2-2 with the relation:

$$T_b = 198 + \Sigma\Delta_b \tag{2-4.1}$$

where T_b is in kelvins. The group increments were developed by Joback [19], and these, with Eq. (2-4.1) were tested on 438 diverse organic compounds. The average absolute error found was 12.9 K, and the standard deviation of the error was 17.9 K. The average of the absolute percent errors was 3.6%. Whereas these errors are not small, this simple technique may be useful as a guide in obtaining approximate values of T_b should no experimental value be available.

Example 2-5   Estimate the normal boiling temperature of isopentylmercaptan. The reported value of T_b is 393 K [4].

solution   From Table 2-2, for this compound we have two $-CH_3$, two $-CH_2$, one $>CH-$, and one $-SH$. $\Sigma\Delta_b = (2)(23.6) + (2)(22.9) + 21.7 + 63.6 = 178.3$

$T_b = 198 + 178 = 376$ K

The error is $376 - 393 = -17$ K.

The estimation of the normal freezing point is complicated by the fact that $T_f = \Delta H_{fus}/\Delta S_{fus}$ and, whereas ΔH_{fus} depends primarily upon intermolecular forces, ΔS_{fus} is a function of the molecular symmetry. As noted by Bondi [7], ΔS_{fus} is larger when the molecule can assume many orientations in the liquid phase relative to the solid. Thus, ΔS_{fus} is smaller for spherical, rigid molecules and T_f is higher than for molecules of the same size which are not spherical and are flexible.

No reliable methods are now available to estimate T_f. For a *very* approximate guess, one may use Eq. (2-4.2) with the group contributions developed by Joback [19] and shown in Table 2-2 under T_f.

$$T_f = 122 + \Sigma\Delta_f \tag{2-4.2}$$

When tested with 388 simple and complex organic compounds, the average absolute error was 23 K with a standard deviation of 25 K. The average of the absolute percent errors was 11%.

Example 2-6 Estimate the normal freezing temperature of 2-bromobutane by using Eq. (2-4.2) and the group contributions in Table 2-2. The experimental value of T_f is 161 K [49].

solution Here we have two $-CH_3$, one $-CH_2-$, one $>CH-$, and one $-Br$. Thus,

$$\Sigma\Delta_f = (2)(-5.1) + 11.3 + 12.6 + 43.4 = 57$$

$$T_f = 122 + 57 = 179 \ K$$

The error is $179 - 161 = 18$ K.

2-5 Dipole Moments

Dipole moments of molecules are often required in property correlations for polar materials. The best source of this constant is the compilation by McClellan [28], which has, to a large degree, superseded prior summaries such as those given by Smith [45] and Smyth [46]. For those rare occasions when one may be forced to estimate a value, there are vector group contribution methods, although they ordinarily require considerable effort. Most such methods are summarized in the text by Minkin et al. [29].

Dipole moments for many materials are listed in Appendix A. No temperature effect is shown, because dipole moments are insensitive to that variable. Also, we have not noted whether the values were measured in the gas phase or in a solvent, because differences between such measurements are ordinarily small.

Dipole moments are expressed in debye units, 1 debye being equivalent to $10^{-18} \ (dyn \cdot cm^4)^{1/2} = 3.162 \times 10^{-25} \ (J \cdot m^3)^{1/2}$. Thus, the physical unit for this property is $[(energy)(volume)]^{1/2}$.

Notation

M	molecular weight
n_A	number of atoms in a molecule
P	pressure, bar; P_c, critical pressure; P_r, reduced pressure, P/P_c; P_{vp}, vapor pressure; P_{vp_r}, P_{vp}/P_c
R	gas constant
T	temperature, kelvins; T_c, critical temperature; T_r, reduced temperature, T/T_c; T_b, normal boiling point (at 1 atm); T_f, freezing point
V	molar volume, cm^3/mol; V_c, critical volume
Z	compressibility factor; Z_c, at the critical point

GREEK

Δ   group contribution. When subscripted by T, for T_c; by P for P_c; by V for V_c; by b for T_b; and by f for T_f

θ T_b/T_c

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Pressure-Volume-Temperature Relations of Pure Gases and Liquids

3-1 Scope

Methods are presented in this chapter for estimating the volumetric behavior of pure gases and liquids as functions of temperature and pressure. Extension to mixtures is given in Chap. 4. Emphasis is placed on equations of state which are applicable to computer-based property-estimation systems.

The equations of state described in this chapter are employed in Chap. 5 to determine thermodynamic departure functions and partial molar properties.

3-2 Two-Parameter Correlations

The nonideality of a gas is conveniently expressed by the compressibility factor Z:

$$Z = \frac{PV}{RT} \tag{3-2.1}$$

where V = molar volume
P = absolute pressure
T = absolute temperature
R = universal gas constant

The gas constant R assumes different values for different sets of units. Common values are shown in Table 3-1. For the remainder of this book, unless otherwise noted, pressure will be in bars, volume in cm^3/mol, and the term mol will refer to gram moles. Note that 1 bar = 10^5 Pa = 10^5 N/m^2 and 1 atm = 1.01325 bar. For an ideal gas Z = 1.0. For real gases, Z is normally less than 1 except at high reduced temperatures and pressures. Equation (3-2.1) can also be used to define Z for a liquid; in this case Z is normally much less than unity.

The compressibility factor is often correlated with the reduced temperature T_r and pressure P_r as

$$Z = f(T_r, P_r) \qquad (3\text{-}2.2)$$

where $T_r = T/T_c$ and $P_r = P/P_c$. The function $f(\ )$ has been obtained from experimental PVT data by Nelson and Obert [73], and the final curves are shown in Figs. 3-1 to 3-3. Except as noted below, the use of these figures to obtain Z at a given T_r and P_r should lead to errors of less than 4 to 6 percent except near the saturation curve or near the critical point, where Z is very sensitive to both T_r and P_r.

Figures 3-1 and 3-3 should not be used for strongly polar fluids, nor are they recommended for helium, hydrogen, or neon unless special, modified critical constants are used [28, 62, 69, 74]. For very high pressures or very high temperatures, the reduced pressure-temperature-density charts of Breedveld and Prausnitz [9] are useful.

Many graphs similar to those in Figs. 3-1 to 3-3 have been published. All differ somewhat, because each reflects the author's choice of experimental data and how the data are smoothed. Those shown are as accurate as any two-parameter plots published, and they have the added advantage that volumes can be found directly. Note, however, that in these figures

TABLE 3-1   Values of the Gas Constant R

Value of R	Unit† for R
83.144	bar·cm^3/(mol·K)
8.3144	J/(mol·K)
10.732	psia·ft^2/(lb-mol·°R)
82.057	atm·cm^3/(mol·K)

†The unit mol refers to gram moles.
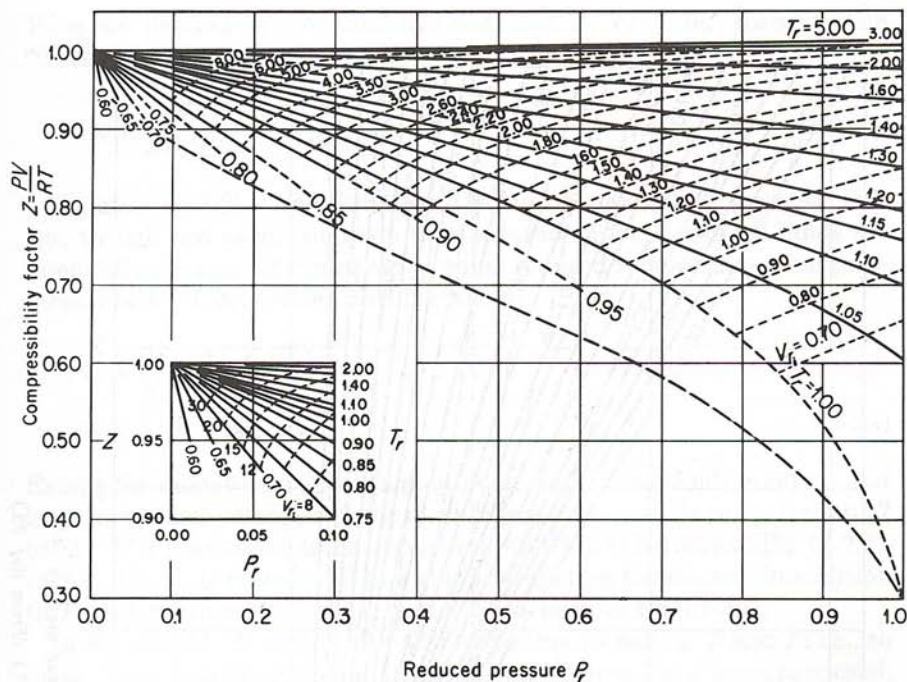
Figure 3-1 Generalized compressibility chart. V_{ri} is $V/(RT_c/P_c)$. *(From Ref. 73.)*
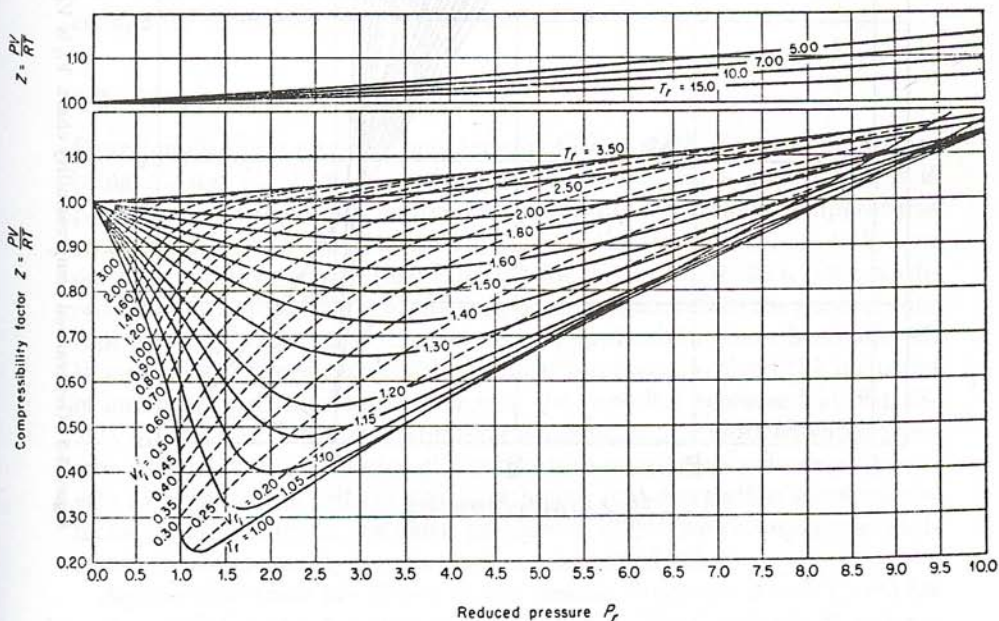
Figure 3-2 Generalized compressibility chart. V_{ri} is $V/(RT_c/P_c)$. *(From Ref. 73.)*
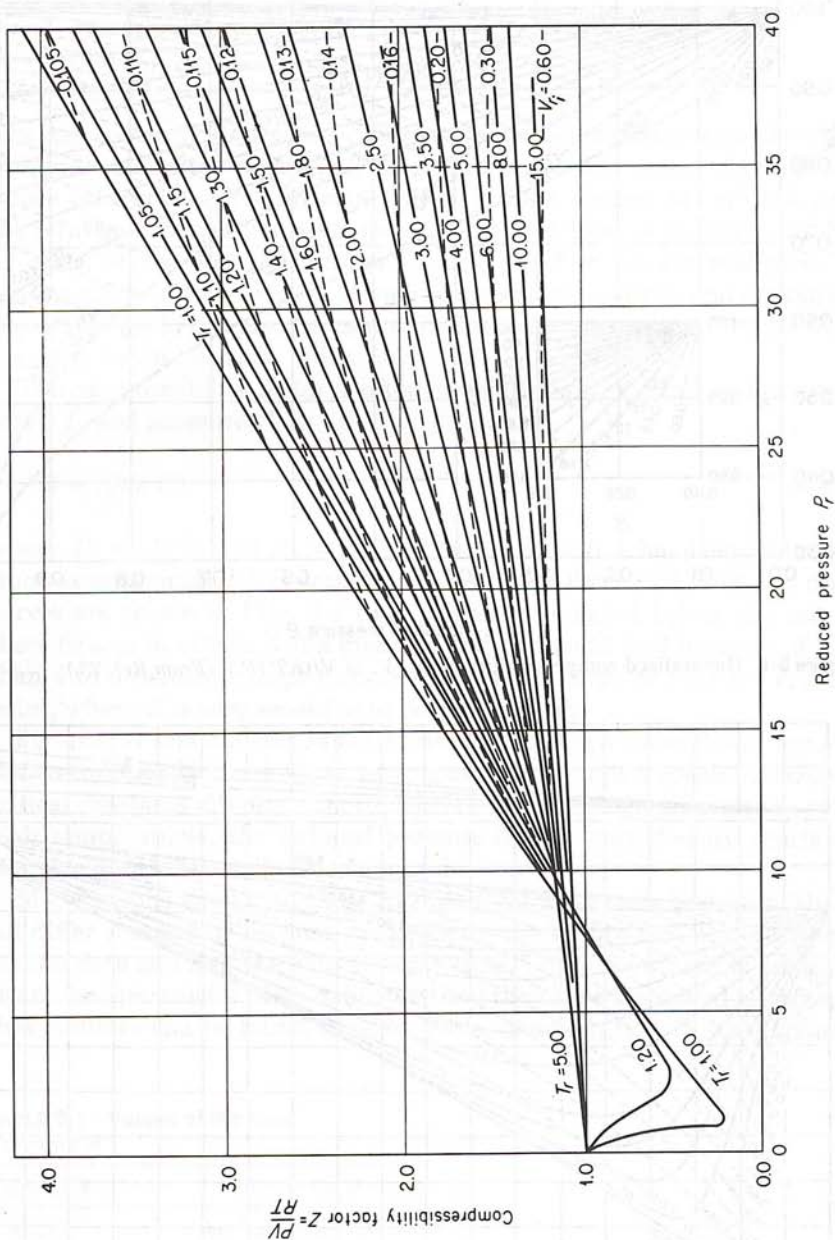
Figure 3-3 Generalized compressibility chart. V_{ri} is $V/(RT_c/P_c)$. (From Ref. 73.)

V_{ri} is not defined in the usual manner, that is, V/V_c, but instead is an "ideal reduced volume" given by

$$V_{ri} = \frac{V}{RT_c/P_c} \tag{3-2.3}$$

Equation (3-2.2) is an example of the law of corresponding states. This law, though not exact, suggests that reduced properties of all fluids are essentially the same if compared at equal reduced temperatures and pressures. For PVT properties, this law gives

$$V_r = \frac{V}{V_c} = \frac{(Z/Z_c)(T/T_c)}{P/P_c} = f_1(T_r, P_r)$$

or

$$Z = Z_c f_2(T_r, P_r) \tag{3-2.4}$$

Except for monatomic gases, highly polar fluids, and fluids composed of large molecules, values of Z_c for most organic compounds range from 0.27 to 0.29. If it is assumed to be a constant, Eq. (3-2.4) reduces to Eq. (3-2.2). In Sec. 3-3, Z_c is introduced as a third correlating parameter (in addition to T_c and P_c) to estimate Z, but not in the form of Eq. (3-2.4).

In Eq. (3-2.2), T_c and P_c are scaling factors to reduce T and P; i.e., to make them nondimensional. Other scaling factors have been proposed, but none have been widely accepted. A tabulation of T_c and P_c for a number of elements and compounds is given in Appendix A, and methods for estimating them are described in Sec. 2-2.

3-3 Three-Parameter Correlations

Equation (3-2.2) is a two-parameter equation of state, the two parameters being T_c and P_c. That is, by knowing T_c and P_c for a given fluid, it is possible to estimate the volumetric properties at various temperatures and pressures. The calculation may involve the use of Figs. 3-1 to 3-3, or one may employ an analytical function for $f(\ )$ in Eq. (3-2.2). Both methods are only approximate. Many suggestions which retain the general concept yet allow an increase in accuracy and applicability have been offered. In general, the more successful modifications have involved the inclusion of an additional third parameter into the function expressed by Eq. (3-2.2). Most often, this third parameter is related to the reduced vapor pressure at some specified reduced temperature or to some volumetric property at or near the critical point, although one correlation employs the molar polarizability as the third parameter [93]. Two common and well-tested three-parameter correlations are described below.

Assume that there are different, but unique, functions $Z = f(T_r, P_r)$ for each group of pure substances with the same Z_c. Then, for each Z_c we have

a different set of Figs. 3-1 to 3-3. All fluids with the same Z_c values then follow the Z-T_r-P_r behavior shown on charts drawn for that particular Z_c. Such a structuring indeed leads to a significant increase in accuracy. This is exactly what was done in the development of the Lydersen-Greenkorn-Hougen tables, which first appeared in 1955 [53] and were later modified [37]. There Z is tabulated as a function of T_r and P_r with separate tables for various values of Z_c. Edwards and Thodos [20] have also utilized Z_c in a correlation to estimate saturated vapor densities of nonpolar compounds.

An alternate third parameter is the Pitzer acentric factor [86–89], defined in Sec. 2-3. This factor is an indicator of the nonsphericity of a molecule's force field; e.g., a value of $\omega = 0$ denotes rare-gas spherical symmetry. Deviations from simple-fluid behavior are evident when $\omega > 0$. Within the context of the present discussion, it is assumed that all molecules with equal acentric factors have identical $Z = f(T_r, P_r)$ functions, as in Eq. (3-2.2). However, rather than prepare separate Z, T_r, P_r tables for different values of ω, it was suggested that a linear expansion could be employed:

$$Z = Z^{(0)}(T_r, P_r) + \omega Z^{(1)}(T_r, P_r) \tag{3-3.1}$$

Thus, the $Z^{(0)}$ function would apply to spherical molecules, and the $Z^{(1)}$ term is a deviation function.

Pitzer et al. tabulated $Z^{(0)}$ and $Z^{(1)}$ as functions of T_r and P_r [89], and Edmister has shown the same values graphically [18]. Several modifications as well as extensions to wider ranges of T_r and P_r have been published [38, 51, 99]. Tables 3-2 and 3-3 list those prepared by Lee and Kesler [47]. The method of calculation is described in Sec. 3-7. With Tables 3-2 and 3-3, Z can be determined for both gases and liquids.* The $Z^{(0)}$ table agrees well with that presented originally by Pitzer et al. over the range of T_r and P_r common to both. The deviation function table of Lee and Kesler (Table 3-3) differs somewhat from that of Pitzer and Curl, but extensive testing [47, 114] indicates the new table is the more accurate.

Tables 3-2 and 3-3 were not intended to be applicable to strongly polar fluids, though they are often so used with surprising accuracy except at low temperatures near the saturated vapor region. Though none have been widely adopted, special techniques have been suggested to modify Eq. (3-3.1) for polar materials [21, 31, 50, 75, 111, 120].

Considerable emphasis has been placed on the Pitzer-Curl generalized relation. It has proved to be accurate and general when applied to pure gases. Only the acentric factor and critical temperature and pressure need

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*For mixtures, see Table 4.3.

be known. It is probably the most successful and useful result of corresponding states theory [48, 109, 110].

Example 3-1 Estimate the specific volume of dichlorodifluoromethane vapor at 20.67 bar and 366.5 K.

solution From Appendix A, $T_c = 385.0$ K, $P_c = 41.4$ bar, and $\omega = 0.204$.

$$T_r = \frac{366.5}{385.0} = 0.952 \qquad P_r = \frac{20.67}{41.4} = 0.499$$

From Fig. 3-1, $Z = 0.77$ and

$$V = \frac{ZRT}{P} = \frac{(0.77)(83.14)(366.5)}{20.67} = 1134 \text{ cm}^3/\text{mol}$$

The value reported in the literature is 1109 cm³/mol [4].

If the Pitzer-Curl method were to be used, from Tables 3-2 and 3-3, $Z^{(0)} = 0.761$ and $Z^{(1)} = -0.082$. From Eq. (3-3.1),

$$Z = 0.761 + (0.204)(-0.082) = 0.744$$

$$V = \frac{ZRT}{P} = 1097 \text{ cm}^3/\text{mol}$$

3-4 Analytical Equations of State

An analytical equation of state is an algebraic relation between pressure, temperature, and molar volume. Three classes of equations of state are presented in the next three sections. The virial equation is discussed in Sec. 3-5. In its truncated form, it is a simple equation, and it can represent only modest deviations in the vapor phase from ideal-gas behavior. In Sec. 3-6, equations which are cubic in volume are discussed. These equations can represent both liquid and vapor behavior of nonpolar molecules over limited ranges of temperature and pressure, and they remain relatively simple from a computational point of view. Section 3-7 describes the Lee-Kesler generalized version of the Benedict-Webb-Rubin equation, which is applicable over broader ranges of temperatures and pressure than are the cubic equations. But it is also computationally more complex.

3-5 Virial Equation

The virial equation of state is a polynomial series in inverse volume which is explicit in pressure and can be derived from statistical mechanics:

$$P = \frac{RT}{V} + \frac{RTB}{V^2} + \frac{RTC}{V^3} + \cdots \qquad (3-5.1)$$

The parameters $B, C, \ldots$ are called the second, third, $\ldots$ virial coefficients and are functions only of temperature for a pure fluid. Much has been written about this particular equation, and several reviews have been pub-

TABLE 3-2   Values of $Z^{(0)}$

T_r	P_r						
	0.010	0.050	0.100	0.200	0.400	0.600	0.800
0.30	0.0029	0.0145	0.0290	0.0579	0.1158	0.1737	0.2315
0.35	0.0026	0.0130	0.0261	0.0522	0.1043	0.1564	0.2084
0.40	0.0024	0.0119	0.0239	0.0477	0.0953	0.1429	0.1904
0.45	0.0022	0.0110	0.0221	0.0442	0.0882	0.1322	0.1762
0.50	0.0021	0.0103	0.0207	0.0413	0.0825	0.1236	0.1647
0.55	0.9804	0.0098	0.0195	0.0390	0.0778	0.1166	0.1553
0.60	0.9849	0.0093	0.0186	0.0371	0.0741	0.1109	0.1476
0.65	0.9881	0.9377	0.0178	0.0356	0.0710	0.1063	0.1415
0.70	0.9904	0.9504	0.8958	0.0344	0.0687	0.1027	0.1366
0.75	0.9922	0.9598	0.9165	0.0336	0.0670	0.1001	0.1330
0.80	0.9935	0.9669	0.9319	0.8539	0.0661	0.0985	0.1307
0.85	0.9946	0.9725	0.9436	0.8810	0.0661	0.0983	0.1301
0.90	0.9954	0.9768	0.9528	0.9015	0.7800	0.1006	0.1321
0.93	0.9959	0.9790	0.9573	0.9115	0.8059	0.6635	0.1359
0.95	0.9961	0.9803	0.9600	0.9174	0.8206	0.6967	0.1410
0.97	0.9963	0.9815	0.9625	0.9227	0.8338	0.7240	0.5580
0.98	0.9965	0.9821	0.9637	0.9253	0.8398	0.7360	0.5887
0.99	0.9966	0.9826	0.9648	0.9277	0.8455	0.7471	0.6138
1.00	0.9967	0.9832	0.9659	0.9300	0.8509	0.7574	0.6353
1.01	0.9968	0.9837	0.9669	0.9322	0.8561	0.7671	0.6542
1.02	0.9969	0.9842	0.9679	0.9343	0.8610	0.7761	0.6710
1.05	0.9971	0.9855	0.9707	0.9401	0.8743	0.8002	0.7130
1.10	0.9975	0.9874	0.9747	0.9485	0.8930	0.8323	0.7649
1.15	0.9978	0.9891	0.9780	0.9554	0.9081	0.8576	0.8032
1.20	0.9981	0.9904	0.9808	0.9611	0.9205	0.8779	0.8330
1.30	0.9985	0.9926	0.9852	0.9702	0.9396	0.9083	0.8764
1.40	0.9988	0.9942	0.9884	0.9768	0.9534	0.9298	0.9062
1.50	0.9991	0.9954	0.9909	0.9818	0.9636	0.9456	0.9278
1.60	0.9993	0.9964	0.9928	0.9856	0.9714	0.9575	0.9439
1.70	0.9994	0.9971	0.9943	0.9886	0.9775	0.9667	0.9563
1.80	0.9995	0.9977	0.9955	0.9910	0.9823	0.9739	0.9659
1.90	0.9996	0.9982	0.9964	0.9929	0.9861	0.9796	0.9735
2.00	0.9997	0.9986	0.9972	0.9944	0.9892	0.9842	0.9796
2.20	0.9998	0.9992	0.9983	0.9967	0.9937	0.9910	0.9886
2.40	0.9999	0.9996	0.9991	0.9983	0.9969	0.9957	0.9948
2.60	1.0000	0.9998	0.9997	0.9994	0.9991	0.9990	0.9990
2.80	1.0000	1.0000	1.0001	1.0002	1.0007	1.0013	1.0021
3.00	1.0000	1.0002	1.0004	1.0008	1.0018	1.0030	1.0043
3.50	1.0001	1.0004	1.0008	1.0017	1.0035	1.0055	1.0075
4.00	1.0001	1.0005	1.0010	1.0021	1.0043	1.0066	1.0090

lished [e.g., 63, 123]. One reason for the equation's popularity is that the coefficients B, C, ... can be related to parameters characterizing the intermolecular potential function. Little information is available for the third and higher virial coefficients. Two methods have, however, appeared recently for predicting C, the third virial coefficient [15, 77]. More often the virial equation is truncated to contain only the second virial coeffi-

			P_r				
1.000	1.200	1.500	2.000	3.000	5.000	7.000	10.000
0.2892	0.3470	0.4335	0.5775	0.8648	1.4366	2.0048	2.8507
0.2604	0.3123	0.3901	0.5195	0.7775	1.2902	1.7987	2.5539
0.2379	0.2853	0.3563	0.4744	0.7095	1.1758	1.6373	2.3211
0.2200	0.2638	0.3294	0.4384	0.6551	1.0841	1.5077	2.1338
0.2056	0.2465	0.3077	0.4092	0.6110	1.0094	1.4017	1.9801
0.1939	0.2323	0.2899	0.3853	0.5747	0.9475	1.3137	1.8520
0.1842	0.2207	0.2753	0.3657	0.5446	0.8959	1.2398	1.7440
0.1765	0.2113	0.2634	0.3495	0.5197	0.8526	1.1773	1.6519
0.1703	0.2038	0.2538	0.3364	0.4991	0.8161	1.1241	1.5729
0.1656	0.1981	0.2464	0.3260	0.4823	0.7854	1.0787	1.5047
0.1626	0.1942	0.2411	0.3182	0.4690	0.7598	1.0400	1.4456
0.1614	0.1924	0.2382	0.3132	0.4591	0.7388	1.0071	1.3943
0.1630	0.1935	0.2383	0.3114	0.4527	0.7220	0.9793	1.3496
0.1664	0.1963	0.2405	0.3122	0.4507	0.7138	0.9648	1.3257
0.1705	0.1998	0.2432	0.3138	0.4501	0.7092	0.9561	1.3108
0.1779	0.2055	0.2474	0.3164	0.4504	0.7052	0.9480	1.2968
0.1844	0.2097	0.2503	0.3182	0.4508	0.7035	0.9442	1.2901
0.1959	0.2154	0.2538	0.3204	0.4514	0.7018	0.9406	1.2835
0.2901	0.2237	0.2583	0.3229	0.4522	0.7004	0.9372	1.2772
0.4648	0.2370	0.2640	0.3260	0.4533	0.6991	0.9339	1.2710
0.5146	0.2629	0.2715	0.3297	0.4547	0.6980	0.9307	1.2650
0.6026	0.4437	0.3131	0.3452	0.4604	0.6956	0.9222	1.2481
0.6880	0.5984	0.4580	0.3953	0.4770	0.6950	0.9110	1.2232
0.7443	0.6803	0.5798	0.4760	0.5042	0.6987	0.9033	1.2021
0.7858	0.7363	0.6605	0.5605	0.5425	0.7069	0.8990	1.1844
0.8438	0.8111	0.7624	0.6908	0.6344	0.7358	0.8998	1.1580
0.8827	0.8595	0.8256	0.7753	0.7202	0.7761	0.9112	1.1419
0.9103	0.8933	0.8689	0.8328	0.7887	0.8200	0.9297	1.1339
0.9308	0.9180	0.9000	0.8738	0.8410	0.8617	0.9518	1.1320
0.9463	0.9367	0.9234	0.9043	0.8809	0.8984	0.9745	1.1343
0.9583	0.9511	0.9413	0.9275	0.9118	0.9297	0.9961	1.1391
0.9678	0.9624	0.9552	0.9456	0.9359	0.9557	1.0157	1.1452
0.9754	0.9715	0.9664	0.9599	0.9550	0.9772	1.0328	1.1516
0.9865	0.9847	0.9826	0.9806	0.9827	1.0094	1.0600	1.1635
0.9941	0.9936	0.9935	0.9945	1.0011	1.0313	1.0793	1.1728
0.9993	0.9998	1.0010	1.0040	1.0137	1.0463	1.0926	1.1792
1.0031	1.0042	1.0063	1.0106	1.0223	1.0565	1.1016	1.1830
1.0057	1.0074	1.0101	1.0153	1.0284	1.0635	1.1075	1.1848
1.0097	1.0120	1.0156	1.0221	1.0368	1.0723	1.1138	1.1834
1.0115	1.0140	1.0179	1.0249	1.0401	1.0747	1.1136	1.1773

cient. The virial equation may also be written as a power series in either V or P, so that truncation leads to two forms. These are

$$Z = 1 + \frac{BP}{RT} \tag{3-5.2a}$$

and

$$Z = 1 + \frac{B}{V} \tag{3-5.2b}$$

TABLE 3-3   Values of $Z^{(1)}$

	P_r						
T_r	0.010	0.050	0.100	0.200	0.400	0.600	0.800
0.30	−0.0008	−0.0040	−0.0081	−0.0161	−0.0323	−0.0484	−0.0645
0.35	−0.0009	−0.0046	−0.0093	−0.0185	−0.0370	−0.0554	−0.0738
0.40	−0.0010	−0.0048	−0.0095	−0.0190	−0.0380	−0.0570	−0.0758
0.45	−0.0009	−0.0047	−0.0094	−0.0187	−0.0374	−0.0560	−0.0745
0.50	−0.0009	−0.0045	−0.0090	−0.0181	−0.0360	−0.0539	−0.0716
0.55	−0.0314	−0.0043	−0.0086	−0.0172	−0.0343	−0.0513	−0.0682
0.60	−0.0205	−0.0041	−0.0082	−0.0164	−0.0326	−0.0487	−0.0646
0.65	−0.0137	−0.0772	−0.0078	−0.0156	−0.0309	−0.0461	−0.0611
0.70	−0.0093	−0.0507	−0.1161	−0.0148	−0.0294	−0.0438	−0.0579
0.75	−0.0064	−0.0339	−0.0744	−0.0143	−0.0282	−0.0417	−0.0550
0.80	−0.0044	−0.0228	−0.0487	−0.1160	−0.0272	−0.0401	−0.0526
0.85	−0.0029	−0.0152	−0.0319	−0.0715	−0.0268	−0.0391	−0.0509
0.90	−0.0019	−0.0099	−0.0205	−0.0442	−0.1118	−0.0396	−0.0503
0.93	−0.0015	−0.0075	−0.0154	−0.0326	−0.0763	−0.1662	−0.0514
0.95	−0.0012	−0.0062	−0.0126	−0.0262	−0.0589	−0.1110	−0.0540
0.97	−0.0010	−0.0050	−0.0101	−0.0208	−0.0450	−0.0770	−0.1647
0.98	−0.0009	−0.0044	−0.0090	−0.0184	−0.0390	−0.0641	−0.1100
0.99	−0.0008	−0.0039	−0.0079	−0.0161	−0.0335	−0.0531	−0.0796
1.00	−0.0007	−0.0034	−0.0069	−0.0140	−0.0285	−0.0435	−0.0588
1.01	−0.0006	−0.0030	−0.0060	−0.0120	−0.0240	−0.0351	−0.0429
1.02	−0.0005	−0.0026	−0.0051	−0.0102	−0.0198	−0.0277	−0.0303
1.05	−0.0003	−0.0015	−0.0029	−0.0054	−0.0092	−0.0097	−0.0032
1.10	−0.0000	0.0000	0.0001	0.0007	0.0038	0.0106	0.0236
1.15	0.0002	0.0011	0.0023	0.0052	0.0127	0.0237	0.0396
1.20	0.0004	0.0019	0.0039	0.0084	0.0190	0.0326	0.0499
1.30	0.0006	0.0030	0.0061	0.0125	0.0267	0.0429	0.0612
1.40	0.0007	0.0036	0.0072	0.0147	0.0306	0.0477	0.0661
1.50	0.0008	0.0039	0.0078	0.0158	0.0323	0.0497	0.0677
1.60	0.0008	0.0040	0.0080	0.0162	0.0330	0.0501	0.0677
1.70	0.0008	0.0040	0.0081	0.0163	0.0329	0.0497	0.0667
1.80	0.0008	0.0040	0.0081	0.0162	0.0325	0.0488	0.0652
1.90	0.0008	0.0040	0.0079	0.0159	0.0318	0.0477	0.0635
2.00	0.0008	0.0039	0.0078	0.0155	0.0310	0.0464	0.0617
2.20	0.0007	0.0037	0.0074	0.0147	0.0293	0.0437	0.0579
2.40	0.0007	0.0035	0.0070	0.0139	0.0276	0.0411	0.0544
2.60	0.0007	0.0033	0.0066	0.0131	0.0260	0.0387	0.0512
2.80	0.0006	0.0031	0.0062	0.0124	0.0245	0.0365	0.0483
3.00	0.0006	0.0029	0.0059	0.0117	0.0232	0.0345	0.0456
3.50	0.0005	0.0026	0.0052	0.0103	0.0204	0.0303	0.0401
4.00	0.0005	0.0023	0.0046	0.0091	0.0182	0.0270	0.0357

For the evaluation of B from experimental data, however, Eq. (3-5.1) should be used, i.e.,

$$B = \lim_{1/V \to 0} \left(\frac{\partial Z}{\partial 1/V} \right)_T \tag{3-5.3}$$

				P_r			
1.000	1.200	1.500	2.000	3.000	5.000	7.000	10.000
-0.0806	-0.0966	-0.1207	-0.1608	-0.2407	-0.3996	-0.5572	-0.7915
-0.0921	-0.1105	-0.1379	-0.1834	-0.2738	-0.4523	-0.6279	-0.8863
-0.0946	-0.1134	-0.1414	-0.1879	-0.2799	-0.4603	-0.6365	-0.8936
-0.0929	-0.1113	-0.1387	-0.1840	-0.2734	-0.4475	-0.6162	-0.8606
-0.0893	-0.1069	-0.1330	-0.1762	-0.2611	-0.4253	-0.5831	-0.8099
-0.0849	-0.1015	-0.1263	-0.1669	-0.2465	-0.3991	-0.5446	-0.7521
-0.0803	-0.0960	-0.1192	-0.1572	-0.2312	-0.3718	-0.5047	-0.6928
-0.0759	-0.0906	-0.1122	-0.1476	-0.2160	-0.3447	-0.4653	-0.6346
-0.0718	-0.0855	-0.1057	-0.1385	-0.2013	-0.3184	-0.4270	-0.5785
-0.0681	-0.0808	-0.0996	-0.1298	-0.1872	-0.2929	-0.3901	-0.5250
-0.0648	-0.0767	-0.0940	-0.1217	-0.1736	-0.2682	-0.3545	-0.4740
-0.0622	-0.0731	-0.0888	-0.1138	-0.1602	-0.2439	-0.3201	-0.4254
-0.0604	-0.0701	-0.0840	-0.1059	-0.1463	-0.2195	-0.2862	-0.3788
-0.0602	-0.0687	-0.0810	-0.1007	-0.1374	-0.2045	-0.2661	-0.3516
-0.0607	-0.0678	-0.0788	-0.0967	-0.1310	-0.1943	-0.2526	-0.3339
-0.0623	-0.0669	-0.0759	-0.0921	-0.1240	-0.1837	-0.2391	-0.3163
-0.0641	-0.0661	-0.0740	-0.0893	-0.1202	-0.1783	-0.2322	-0.3075
-0.0680	-0.0646	-0.0715	-0.0861	-0.1162	-0.1728	-0.2254	-0.2989
-0.0879	-0.0609	-0.0678	-0.0824	-0.1118	-0.1672	-0.2185	-0.2902
-0.0223	-0.0473	-0.0621	-0.0778	-0.1072	-0.1615	-0.2116	-0.2816
-0.0062	0.0227	-0.0524	-0.0722	-0.1021	-0.1556	-0.2047	-0.2731
0.0220	0.1059	0.0451	-0.0432	-0.0838	-0.1370	-0.1835	-0.2476
0.0476	0.0897	0.1630	0.0698	-0.0373	-0.1021	-0.1469	-0.2056
0.0625	0.0943	0.1548	0.1667	0.0332	-0.0611	-0.1084	-0.1642
0.0719	0.0991	0.1477	0.1990	0.1095	-0.0141	-0.0678	-0.1231
0.0819	0.1048	0.1420	0.1991	0.2079	0.0875	0.0176	-0.0423
0.0857	0.1063	0.1383	0.1894	0.2397	0.1737	0.1008	0.0350
0.0864	0.1055	0.1345	0.1806	0.2433	0.2309	0.1717	0.1058
0.0855	0.1035	0.1303	0.1729	0.2381	0.2631	0.2255	0.1673
0.0838	0.1008	0.1259	0.1658	0.2305	0.2788	0.2628	0.2179
0.0816	0.0978	0.1216	0.1593	0.2224	0.2846	0.2871	0.2576
0.0792	0.0947	0.1173	0.1532	0.2144	0.2848	0.3017	0.2876
0.0767	0.0916	0.1133	0.1476	0.2069	0.2819	0.3097	0.3096
0.0719	0.0857	0.1057	0.1374	0.1932	0.2720	0.3135	0.3355
0.0675	0.0803	0.0989	0.1285	0.1812	0.2602	0.3089	0.3459
0.0634	0.0754	0.0929	0.1207	0.1706	0.2484	0.3009	0.3475
0.0598	0.0711	0.0876	0.1138	0.1613	0.2372	0.2915	0.3443
0.0565	0.0672	0.0828	0.1076	0.1529	0.2268	0.2817	0.3385
0.0497	0.0591	0.0728	0.0949	0.1356	0.2042	0.2584	0.3194
0.0443	0.0527	0.0651	0.0849	0.1219	0.1857	0.2378	0.2994

As the density approaches zero, Eqs. (3-5.2a) and (3-5.2b) become identical, and at low densities, both forms of Eq. (3-5.2) approximate true behavior. But neither Eq. (3-5.2a) nor (3-5.2b) should be used if $\rho > \rho_c/2$ or if V_{r_i} as defined in Figs. 3-1 to 3-3 is less than about 0.5. When $\rho = \rho_c/2$, Eq. (3-5.2a) predicts a Z which is too high and Eq. (3-5.2b) predicts

a Z which is too low [128]; Eq. (3-5.2a) is easier to use and is thus preferred over Eq. (3-5.2b). If two virial coefficients are retained, the preferred form is that given in Eq. (3-5.1).

Since B is a function only of temperature, Eq. (3-5.2a) predicts that Z is a linear function of pressure along an isotherm. Examination of Fig. 3-1 shows that this is not a bad assumption at low values of P_r.

A compilation of second virial coefficients is given by Dymond and Smith [17]. To estimate values, a number of techniques are available. Most are based on the integration of a theoretical expression relating intermolecular energy to the distance of separation between molecules. With our present limited ability to determine such energies, however, it is more common to employ corresponding states relations to estimate B.

For nonpolar molecules [128],

$$\frac{BP_c}{RT_c} = B^{(0)} + \omega B^{(1)} \tag{3-5.4}$$

$$B^{(0)} = 0.083 - \frac{0.422}{T_r^{1.6}} \tag{3-5.5}$$

$$B^{(1)} = 0.139 - \frac{0.172}{T_r^{4.2}} \tag{3-5.6}$$

In Fig. 3-4, Eq. (3-5.3) is shown to correlate well experimental second virial coefficient data for 14 nonpolar fluids. Except at high temperatures, B is negative; by Eq. (3-5.2), the compressibility factor is less than unity.

Equation (3-5.4) should be considered applicable only for nonpolar or slightly polar materials. For polar molecules, Tsonopoulos [121] recom-
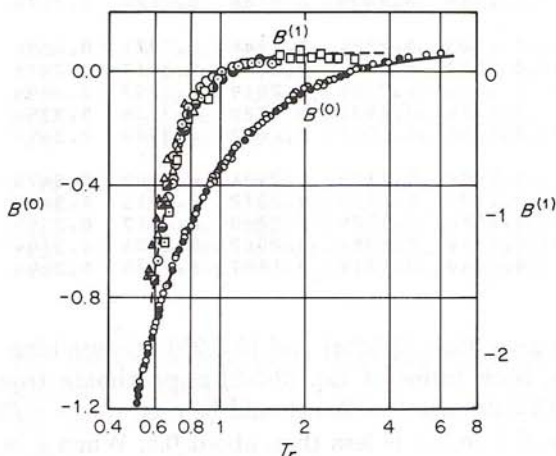
Figure 3-4 Second virial coefficient for 14 nonpolar fluids; Eqs. (3-5.5) and (3-5.6) (*From Ref. 128.*)

TABLE 3-4   Values of a and b for Eq. (3-5.7) [121, 122, 124]

Compound class	a	b
Ketones, aldehydes, nitriles, ethers, NH_3, H_2S, HCN, esters	$\dfrac{-2.112 \times 10^{-4}\,\mu_r\dagger - 3.877 \times 10^{-21}}{\mu_r^8}$	0
Mercaptans	0	0
Monoalkyhalides	$2.076 \times 10^{-11}\,\mu_r^4 - 7.048 \times 10^{-21}\,\mu_r^8$	
Alcohols	0.0878	0.04 − 0.06‡
Phenol	−0.0136	0

†μ_r is defined in Eq. (3-5.8).
‡See Ref. 121 for specific values.

mends that Eq. (3-5.4) be modified by the addition of another term $B^{(2)}$, where

$$B^{(2)} = \frac{a}{T_r^6} - \frac{b}{T_r^8} \qquad (3\text{-}5.7)$$

Neither a nor b can be estimated with much accuracy; Tsonopoulos [121, 122, 124], however, has correlated a and b for several compound classes. b is zero for nonhydrogen-bonded materials, and a is given by the values or expressions in Table 3-4. These expressions are functions of the reduced dipole moment,

$$\mu_r = \frac{10^5 \mu^2 P_c}{T_c^2} \qquad (3\text{-}5.8)$$

where μ = dipole moment, debyes
  P_c = critical pressure, bars
  T_c = critical temperature, K

Example 3-2 Estimate the second virial coefficient of methyl isobutyl ketone at 120°C.

solution From Appendix A, $T_c = 571$ K, $P_c = 32.7$ bar, $\omega = 0.385$, and $\mu = 2.8$ debyes. With $T_r = (120 + 273)/571 = 0.689$ and with Eqs. (3-5.5) and (3-5.6), $B^{(0)} = -0.684$ and $B^{(1)} = -0.684$, and with Eq. (3-5.8) $\mu_r = (10^5)(2.8)^2(32.7/571^2)$ = 78.6. From Table 3-4 and Eq. (3-5.7) $a = 0.0166$ and $B^{(2)} = -0.155$. Since methyl isobutyl ketone is nonhydrogen-bonded, $b = 0$. Then, using Eqs. (3-5.4) and (3-5.7),

$$\frac{(B)(32.7)}{(83.14)(571)} = -0.684 + (0.385)(-0.686) + (-0.155)$$

$$B = -1601 \text{ cm}^3/\text{mol}$$

The experimental value is -1580 cm³/mol [35].

Several other methods have been proposed for estimating B for polar compounds [36, 91, 108, 113]. Values of the parameters used in the Hayden-O'Connell method for a number of compounds and a summary of the equations are given in Ref. 94. A technique for treating compounds that associate, such as acetic acid, is also given in Ref. 94. More recently, McCann and Danner [66] have developed a rather involved group contribution method for second virial coefficients. Their method requires only the critical temperature, and except for organic acids it reproduces all existing data to an accuracy equivalent to that of the Tsonopoulos method. The McCann-Danner method can be used for new compounds for which very little information is available, but it has not been tested for mixtures.

3-6 Cubic Equations of State

The term "cubic equation of state" implies an equation which, if expanded, would contain volume terms raised to either the first, second, or third power. Many of the common two-parameter cubic equations can be expressed by the equation

$$P = \frac{RT}{V - b} - \frac{a}{V^2 + ubV + wb^2} \tag{3-6.1}$$

An equivalent form of Eq. (3-6.1) is

$$Z^3 - (1 + B^* - uB^*)Z^2 + (A^* + wB^{*2} - uB^* - uB^{*2})Z \tag{3-6.2}$$
$$- A^*B^* - wB^{*2} - wB^{*3} = 0$$

where

$$A^* = \frac{aP}{R^2T^2} \tag{3-6.3}$$

and

$$B^* = \frac{bP}{RT} \tag{3-6.4}$$

Four well-known cubic equations are the van der Waals, Redlich-Kwong (RK) [96], Soave (SRK) [101], and Peng-Robinson (PR) [84] equations. For these four equations, u and w take on the integer values listed in Table 3-5. There are several approaches which have been used to set the values of the two parameters, a and b, that appear in Eq. (3-6.1). One approach is to choose a and b so that the two critical point conditions

$$\left(\frac{\partial P}{\partial V}\right)_{T_c} = 0 \tag{3-6.5}$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c} = 0 \tag{3-6.6}$$

TABLE 3-5   Constants for Four Common Cubic Equations of State

Equation	u	w	b	a
van der Waals	0	0	$\dfrac{RT_c}{8P_c}$	$\dfrac{27}{64}\dfrac{R^2T_c^2}{P_c}$
Redlich-Kwong	1	0	$\dfrac{0.08664RT_c}{P_c}$	$\dfrac{0.42748R^2T_c^{2.5}}{P_cT^{1/2}}$
Soave	1	0	$\dfrac{0.08664RT_c}{P_c}$	$\dfrac{0.42748R^2T_c^2}{P_c}[1+f\omega(1-T_r^{1/2})]^2$ where $f\omega = 0.48 + 1.574\omega - 0.176\omega^2$
Peng-Robinson	2	−1	$\dfrac{0.07780RT_c}{P_c}$	$\dfrac{0.45724R^2T_c^2}{P_c}[1+f\omega(1-T_r^{1/2})]^2$ where $f\omega = 0.37464 + 1.54226\omega - 0.26992\omega^2$

are satisfied. Eqs. (3-6.5) and (3-6.6) are applicable only to pure compo-
nents. Both Soave and Peng and Robinson used Eqs. (3-6.5) and (3-6.6)
to find a and b at the critical point. They then made the parameter a a
function of temperature and acentric factor so as to reproduce hydrocar-
bon vapor pressures. The expresssions for a and b which result from this
procedure are listed in Table 3-5. Graboski and Daubert [26] have given
a slightly different expression for $f\omega$ in the SRK equation.

An alternative approach to the determination of a and b in Eq. (3-6.1)
is that first suggested by Joffe et al. [39]. In this approach, both a and b
are functions of temperature and can be set so as to reproduce some
selected pure component data. This technique has been extended by var-
ious workers, and temperature-dependent values of a and b have been
published [12, 32, 134]. If the two conditions, saturated liquid volume and
vapor pressure, are used to set a and b, then Eq. (3-6.1) will reproduce
exactly these two pure component properties. For this case, Panagioto-
poulos and Kumar [80] have shown that a and b can be calculated
approximately by

$$b = \frac{RTZ^L}{P}\frac{\sum_i A_i(\ln Z^L)^i}{1+\sum_i A_i(\ln Z^L)^i} \tag{3-6.7}$$

$$a = bRT\sum_i B_i(\ln Z^L)^i \tag{3-6.8}$$

Z^L is the compressibility factor for the pure saturated liquid. The coeffi-
cients A_i and B_i are given in Table 3-6. Morris and Turek [70] have used
the vapor pressure and volumetric data over a range of pressures (at a
fixed temperature) to determine optimal values of a and b for eight sub-

TABLE 3-6   Coefficients for Eqs. (3-6.7) and (3-6.8)

i	$6.91 \times 10^{-13} \le Z^L \le 0.011$		$0.011 \le Z^L \le Z_c$	
	A_i	B_i	A_i	B_i
	Redlich-Kwong (or Soave) Form ($u = 1, w = 0$)			
0	-0.874084	1.50479	-3.66182×10^{-2}	5.88848
1	-0.827262	-1.66630	-0.203841	2.07104
2	-1.74216×10^{-3}	-6.30280×10^{-3}	0.147671	1.31927
3	—	-7.68315×10^{-5}	1.19456×10^{-2}	0.226604
4	—	—	—	1.52897×10^{-2}
	Peng-Robinson Form ($u = 2, w = -1$)			
0	-1.21190	1.82378	2.14469×10^{-2}	7.09646
1	-0.918850	-1.84430	-5.87391×10^{-2}	2.41021
2	-1.91042×10^{-3}	-5.75993×10^{-3}	0.195961	1.41294
3	—	-2.90784×10^{-5}	1.53575×10^{-2}	0.229028
4	—	8.43108×10^{-7}	—	1.47396×10^{-2}

stances. Their results are shown in Fig. 3-5 for CO_2. The volumetric behavior predicted with the a and b from Table 3-5 for the RK and SRK equations is shown in Figs. 3-6 and 3-7. Figure 3-7 indicates that the original RK equation gives more accurate volume behavior for T_r and P_r greater than 1. This is expected because the Soave a parameter was fit to vapor pressure data which don't exist above $T_r = 1$. Thus, the Soave equation should not be used at large reduced temperatures. Results with the Morris-Turek parameters shown in Fig. 3-5 demonstrate better volume behavior than either the RK or SRK equation because the area with errors greater than 10 percent (located at $P_r \sim 1.4$ and $T_r \sim 1.01$) is very small.
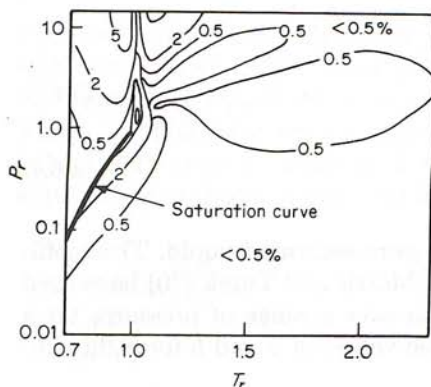
Figure 3-5 Percent error in molar volume calculated for CO_2 by using the Redlich-Kwong equation of state with Morris-Turek parameters.
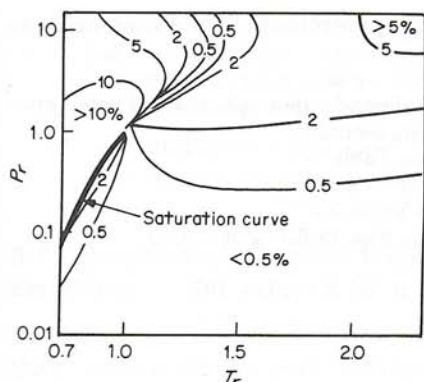
Figure 3-6 Percent error in molar volume calculated for CO_2 by using the Redlich-Kwong equation of state with standard parameters.

There have been numerous modifications of cubic equations to improve their predictions of liquid volumes, most of which involve a third parameter [24, 34, 100, 127] in addition to the a and b already in Eq. (3-6.1). Peneloux and Rauzy [83] have correlated the errors in the liquid volumes as predicted by the Soave equation at $T_r = 0.7$ and recommend that the following correction be subtracted from the volume obtained in the SRK equation

$$c = 0.40768(0.29441 - Z_{RA}) \frac{RT_c}{P_c} \tag{3-6.9}$$

Z_{RA} is the Rackett compressibility factor appearing in Spencer and Danner's [106] modification of the Rackett equation (Sec. 3-11). In terms of a new equation of state, Eq. (3-6.9) represents a volume translation which has no effect on the VLE behavior predicted by the SRK equation. This concept would allow one to fit a and b in the original cubic equation with
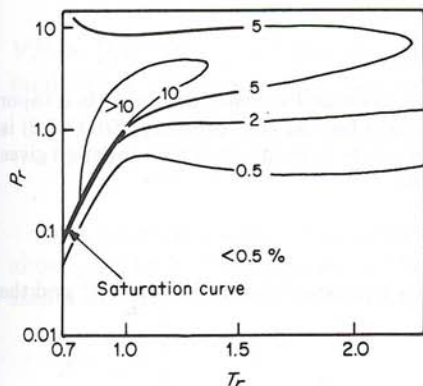
Figure 3-7 Percent error in molar volume calculated for CO_2 by using the Redlich-Kwong equation of state with Soave parameters.

vapor pressures and vapor volumes. The parameter c could then be fit so as to reproduce liquid volumes [54].

Example 3-3 Calculate the saturated liquid and vapor volumes and vapor pressure of isobutane at 300 K by the following methods:
(a) The SRK equation with a and b from Table 3-5
(b) Peneloux's correction to the results from part (a)
(c) The PR equation with a and b from Table 3-5
(d) The SRK equation with a and b from Eqs. (3-6.7) and (3-6.8)

Literature values and data for isobutane at 300 K are [14, 107]
    Vapor pressure = 3.704 bar
$$V^L = 105.9 \text{ cm}^3/\text{mol}$$
$$V^V = 6031 \text{ cm}^3/\text{mol}$$

From Appendix A, $T_c = 408.2$ K, $P_c = 36.5$ bar, and $\omega = 0.183$. Also, $Z_{RA} = 0.27569$ [105].

solution

(a) The vapor pressure is the pressure at which the fugacity coefficient for the liquid, ϕ^L, is equal to the fugacity coefficient for the vapor, ϕ^V. An iterative process whereby one guesses P, solves Eq. (3-6.2) for Z^L and Z^V, calculates ϕ^L and ϕ^V with the equations in Chap. 5, and adjusts P by $P_{\text{new}} = P_{\text{old}}\phi^L/\phi^V$ leads to the result that the predicted vapor pressure is 3.706 bar. At that pressure, Eq. (3-6.2) is $Z^3 - Z^2 + 0.08668Z - 0.0011825 = 0$. This may be solved analytically for the largest and smallest values of Z to give $Z^L = 0.01687$ and $Z^V = 0.9057$. Then

$$V^L = (0.01687)\,\frac{(83.14)(300)}{3.706}$$

$$V^L = 113.5 \text{ cm}^3/\text{mol (7.2\% error)}$$

Similarly

$$V^V = 6096 \text{ cm}^3/\text{mol (1.1\% error)}$$

(b) Equation (3-6.9) gives

$$c = (0.40768)(83.14)(408.2)(0.29441 - 0.27569)/(36.5)$$
$$c = 7.1 \text{ cm}^3/\text{mol}$$
$$V^L = 113.5 - 7.1$$
$$V^L = 106.4 \text{ cm}^3/\text{mol (0.5\% error)}$$
$$V^V = 6089 \text{ cm}^3/\text{mol (0.6\% error)}$$

(c) The PR equation, by the procedure described in part (a), predicts a vapor pressure for isobutane at 300 K of 3.683 bar. At that pressure, Eq. (3-6.2) is $Z^3 - 0.9893Z^2 + 0.08025Z - 0.0009738 = 0$. Solution of this equation gives $Z^L = 0.01479$ and $Z^V = 0.9015$. Thus

$$V^L = 100.2 \text{ cm}^3/\text{mol (5.4\% error)}$$
$$V^V = 6105 \text{ cm}^3/\text{mol (1.2\% error)}$$

(d) Equations (3-6.7) and (3-6.8) require the experimental values of Z^L and the vapor pressure

$$Z^L = \frac{(3.704)(105.9)}{(83.14)(300)} = 0.01573$$

Equations (3-6.7) and (3-6.8) give $b = 75.66$ cm^3/mol and $a = 1.577 \times 10^7$ bar$\cdot$cm^6/mol^2. These constants, along with the procedure described in part (a), predict a vapor pressure for isobutane at 300 K of 3.711 bar. The liquid and vapor compressibility factors are 0.01577 and 0.9104 respectively. Thus,

$$V^L = 106.0 \text{ cm}^3/\text{mol} \ (0.1\% \text{ error})$$
$$V^V = 6119 \text{ cm}^3/\text{mol} \ (1.5\% \text{ error})$$

3-7 Generalized Benedict-Webb-Rubin Equations

The Benedict-Webb-Rubin (BWR) equation of state is more complicated than cubic equations, and it has been used with success over wide ranges of temperature and pressure. Constants for the BWR equation for a number of pure compounds have been tabulated [13, 78, 85]. The success of the original Benedict-Webb-Rubin equation has led to a number of studies wherein the equation or a modification of it has been generalized to apply to many types of compounds [19, 76, 112, 132].

Lee and Kesler [47] developed a modified BWR equation within the context of Pitzer's three-parameter correlation. To employ the analytical form, care must be taken in the method of solution. The compressibility factor of a real fluid is related to properties of a simple fluid ($\omega = 0$) and those of n-octane as a reference fluid. Assume that Z is to be calculated for a fluid at some temperature and pressure. First, using the critical properties of this fluid, determine T_r and P_r. Then determine an ideal reduced volume of a simple fluid with Eq. (3-7.1).

$$\frac{P_r V_r^{(0)}}{T_r} = 1 + \frac{B}{V_r^{(0)}} + \frac{C}{(V_r^{(0)})^2} + \frac{D}{(V_r^{(0)})^5}$$
$$+ \frac{c_4}{T_r^3 (V_r^{(0)})^2} \left[\beta + \frac{\gamma}{(V_r^{(0)})^2} \right] \exp \left[- \frac{\gamma}{(V_r^{(0)})^2} \right]$$

(3-7.1)

where $\quad B = b_1 - \dfrac{b_2}{T_r} - \dfrac{b_3}{T_r^2} - \dfrac{b_4}{T_r^3} \quad C = c_1 - \dfrac{c_2}{T_r} + \dfrac{c_3}{T_r^3} \quad D = d_1 + \dfrac{d_2}{T_r}$

$V_r^{(0)} = P_c V^{(0)}/RT_c$, and the constants are given in Table 3-7 for a simple fluid. With $V_r^{(0)}$, the simple fluid compressibility factor is calculated.

$$Z^{(0)} = \frac{P_r V_r^{(0)}}{T_r}$$

(3-7.2)

Next, using the same reduced temperature and pressure as determined above, Eq. (3-7.1) is again solved for $V_r^{(0)}$ but with the reference fluid constants in Table 3-7; call this value $V_r^{(R)}$. Then

$$Z^{(R)} = \frac{P_r V_r^{(R)}}{T_r}$$

(3-7.3)

TABLE 3-7 Lee-Kesler Constants for Eq. (3-7.1)

Constant	Simple fluid	Reference fluid	Constant	Simple fluid	Reference fluid
b_1	0.1181193	0.2026579	c_3	0.0	0.016901
b_2	0.265728	0.331511	c_4	0.042724	0.041577
b_3	0.154790	0.027655	$d_1 \times 10^4$	0.155488	0.48736
b_4	0.030323	0.203488	$d_2 \times 10^4$	0.623689	0.0740336
c_1	0.0236744	0.0313385	β	0.65392	1.226
c_2	0.0186984	0.0503618	γ	0.060167	0.03754

The compressibility factor Z for the fluid of interest is then calculated

$$Z = Z^{(0)} + \left(\frac{\omega}{\omega^{(R)}}\right)(Z^{(R)} - Z^{(0)}) \tag{3-7.4}$$

where $\omega^{(R)} = 0.3978$.

Equation (3-7.4) was used to generate the $Z^{(0)}$ and $Z^{(1)}$ values in Tables 3-2 and 3-3. Although tested primarily on hydrocarbons, average errors normally were less than 2 percent for both the vapor and liquid phases. The reduced-temperature range is 0.3 to 4, and the reduced-pressure range is 0 to 10. The application of Lee-Kesler equations to mixtures is covered in Sec. 4-6 and to thermodynamic properties in Sec. 5-4.

Starling and coworkers [7, 129, 130] have also developed a generalized BWR equation. As in the Lee-Kesler equation, Starling's version retains the density dependence given in the original BWR equation. Starling uses a third parameter, an "orientation parameter," which is similar to but not identical with the Pitzer acentric factor. Although Starling's equation and its performance are generally similar to the Lee-Kesler equation, it has been more extensively tested for coal-derived compounds. McFee et al. [67] have compared the Starling and Lee-Kesler equations and found they gave similar results. For one-time calculations the Lee-Kesler method is easier to use because Tables 3-2 and 3-3 are available. Twu [125] has recast the Starling equation into a form such that only the normal boiling point is required as a parameter and has successfully reproduced properties for the paraffins methane through n-hectane ($C_{100}H_{202}$).

The Pitzer approach to three-parameter corresponding states theory assumes that the compressibility factor Z depends linearly on the acentric factor ω. In Eq. (3-7.4), the two points used to establish this straight line are the Z values of a simple fluid and the reference fluid, n-octane. There is nothing special about these two reference fluids and, in fact, any two fluids could be used as reference fluids. In this case, Eq. (3-7.4) takes the form [117]

$$Z = Z^{(R1)} + \frac{\omega - \omega^{(R1)}}{\omega^{(R2)} - \omega^{(R1)}}(Z^{(R2)} - Z^{(R1)}) \tag{3-7.5}$$

In the application of Eq. (3-7.5) the Z values for the two reference fluids and the fluid of interest are all evaluated at the same reduced temperature and pressure. In the Lee-Kesler method, the reference fluid properties were expressed by Eqs. (3-7.1) to (3-7.3), but, in general, any equation which satisfactorily represented the reference fluid behavior could be used. Thus, Teja et al. [118] used a cubic equation of state while others [65, 81] have used a 35-term extended BWR equation.

3-8 Discussion of Equations of State

In this section, the equations of state previously presented are compared. In the low-density limit, all reduce to the ideal-gas law. In the critical region, none of the equations is satisfactory. The primary differences occur with respect to computational simplicity and to the quality of the results at high pressures, for the liquid phase, and for polar molecules. Historically, equations of state have been used to represent the behavior of only vapor phases. More recently, they have been used for the liquid phase as well. Thus, it is desirable to have an equation of state that represents the PVT behavior of both vapor and liquid phases. It is necessary to strive for an equation that can be extended to mixtures and generate accurate mixture enthalpies and phase equilibria results. Finally, it is desirable that the equation remain relatively simple from a computational point of view. Of course, to have all of these is not possible.

The truncated virial equation, Eq. (3-5.2) is simple but can be used only for the vapor phase, and then only for modest deviations from ideal-gas behavior, i.e., if the reduced density is less than $\frac{1}{2}$. Temperatures and pressures for which that condition applies can be identified as the regions in Figs. 3-1 to 3-3 for which V_{ri} is greater than but about 0.5.

Both the cubic equations in Sec. 3-6 and the generalized BWR equations in Sec. 3-7 are capable of representing liquid phase behavior. The BWR-based equations are applicable over broader temperature and pressure ranges; cubic equations are less complex. It is possible, and generally recommended, to solve cubic equations for volume (or equivalently, the compressibility factor) noniteratively. The BWR equations must be solved iteratively. Specific computational problems encountered with both types of equations have been discussed [27, 40, 90, 92]; see also Sec. 8-12. All the cubic equations of state in Table 3-5 are of the van der Waals form

$$P = P_{\text{repulsive}} + P_{\text{attractive}} \tag{3-8.1}$$

This idea, that the pressure of a fluid results from the sum of repulsive and attractive forces, was first expressed by van der Waals in his equation. In most cubic equations, the repulsive part is represented by $RT/(V-b)$. This gives only a qualitative description of the repulsive behavior of molecules. But cubic equations can give good results, which means that the repulsive and attractive contributions are not truly separated. Thus, even though cubic equations are effective for curve fitting PVT behavior of fluids, they should not be extrapolated outside the regions of fitted data, especially to high pressures. Efforts to extend the range of applicability of cubic equations have met with some success [34, 41, 43]. However, there are certain limitations that result because the density dependence can be

no more complicated than cubic; these limitations have been discussed by Abbott [1, 2] and Martin [55–61].

The modified BWR equations are similar to the cubic equations in the sense that they should not be extrapolated outside the temperature and pressure ranges for which they have been tested. Within those ranges, they do very well, however; in fact, one of their primary advantages is that they have been tested extensively for many hydrocarbons and coal-derived compounds and with respect to almost all thermodynamic properties.

Neither cubic equations nor BWR equations can be used to *predict*, with confidence, the *PVT* behavior of polar molecules. That is consistent with the fact that polar molecules often do not obey three-parameter corresponding states theory. An equation of state presented by Gmehling et al. [25, 26a] has been used with some success, but the equation requires four pure component parameters which must be determined from experimental data. The equation allows pure components to dimerize and predicts changes in pure component molar volumes because the apparent number of moles changes (with reaction). This approach is particularly effective for compounds like acetic acid which are known to dimerize, even in the vapor phase.

Wu and Stiel [131a] have extended the Lee-Kesler method to polar compounds by the addition of a term to Eq. (3-3.1)

$$Z = Z^{(0)} + \omega Z^{(1)} + Y Z^{(2)} \tag{3-8.2}$$

Y is a polar parameter unique to each compound, and water is used as a reference fluid to determine values of $Z^{(2)}$. Wu and Stiel tabulate values of Y for several compounds, and they give values of $Z^{(2)}$ as functions of T_r and P_r. Errors in compressibility factor predictions for several polar compounds were reduced from 10 to 1 percent by the addition of the term $Y Z^{(2)}$. To date, Eq. (3-8.2) has not been tested for highly associated compounds (acetic acid, for example), nor has it been tested for mixtures. A different form is required for alcohols [131a].

Recommendations

To characterize small deviations from ideal-gas behavior, use the truncated virial equation, Eq. (3-5.2). Do not use the virial equation for the liquid phase.

For nonpolar molecules near saturated conditions, use the Soave or Peng-Robinson equation of state; use Peneloux's correction to the Soave equation to obtain more accurate liquid volumes. The Peng-Robinson equation is essentially equivalent to the Soave equation for saturated vapors.

For expanded ranges of temperature and pressure, use the Lee-Kesler method or Starling's equation. The Gmehling equation is recommended for polar molecules if the parameters are available. All three of these equations are capable of representing the liquid phase accurately. However, if one wishes to calculate only liquid volumes, one of the correlations in the following sections is recommended.

3-9   *PVT* Properties of Liquids—General Considerations

Liquid specific volumes are relatively easy to measure. For most common organic liquids, at least one experimental value is available. There are a number of references in which these experimental volumes (or densities) are tabulated or in which constants are given to allow one to calculate them rapidly with an empirical equation [3, 16, 23, 49, 64, 68, 72, 115, 131]. References 30 and 116 are extensive bibliographies for liquid *PVT* data published to 1978 and 1983 respectively. Ritter, Lenoir, and Schweppe [97] have published convenient nomographs to estimate saturated liquid densities as functions of temperature for some 90 liquids covering, primarily, hydrocarbons and hydrocarbon derivatives. In Appendix A, single-liquid densities are tabulated for many compounds at a given temperature.

3-10   Estimation of the Liquid Molar Volume at the Normal Boiling Point

A number of additive methods are discussed by Partington [82]. Each element and certain bond linkages are assigned numerical values, so that the molar volume at the normal boiling point can be calculated by the addition of these values in a manner similar to that described in Chap. 2 for estimating the critical volume.

Additive methods

Schroeder [82] has suggested a novel and simple additive method for estimating molar volumes at the normal boiling point. His rule is to count the number of atoms of carbon, hydrogen, oxygen, and nitrogen, add 1 for each double bond, and multiply the sum by 7. This gives the volume in cubic centimeters per mole. His rule is surprisingly good: it gives results within 3 to 4 percent except for highly associated liquids. Table 3-8 gives the values to be used with these and other atoms and functional groups. The accuracy of Schroeder's method is shown in Table 3-9, where molar volumes at the normal boiling point are compared with experimental values for a wide range of materials. The average error for the compounds

TABLE 3-8   Volume Increments for the Calculation of Molar Volumes V_b

	Increment, cm³/mol	
	Schroeder	Le Bas
Carbon	7	14.8
Hydrogen	7	3.7
Oxygen (except as noted below)	7	7.4
In methyl esters and ethers	—	9.1
In ethyl esters and ethers	—	9.9
In higher esters and ethers	—	11.0
In acids	—	12.0
Joined to S, P, or N	—	8.3
Nitrogen	7	
Doubly bonded	—	15.6
In primary amines	—	10.5
In secondary amines	—	12.0
Bromine	31.5	27
Chlorine	24.5	24.6
Fluorine	10.5	8.7
Iodine	38.5	37
Sulfur	21	25.6
Ring, three-membered	−7	−6.0
Four-membered	−7	−8.5
Five-membered	−7	−11.5
Six-membered	−7	−15.0
Naphthalene	−7	−30.0
Anthracene	−7	−47.5
Double bond between carbon atoms	7	—
Triple bond between carbon atoms	14	—

tested is 3.0 percent. (Schroeder's original rule has been expanded to include halogens, sulfur, and triple bonds.)

Additive volumes published by Le Bas [44] represent a refinement of Schroeder's rule. Volume increments from Le Bas are shown in Table 3-8, and calculated values of V_b are also compared with experimental values in Table 3-9. The average error for the compounds tested is 4.0 percent. Although the average error in this case is greater than that found by Schroeder's increments, the method appears to be more general and as accurate as Schroeder's for most of the compounds tested; i.e., the average error is not particularly representative.

Other additive methods are discussed by Fedors [22].

Tyn and Calus method [126]

V_b is related to the critical volume by

$$V_b = 0.285 \, V_c^{1.048}$$

(3-10.1)

TABLE 3-9   Comparison of Calculated and Experimental Liquid Molar Volumes at the Normal Boiling Point

Compound	Molar volume, cm³/mol		Percent error† when calculated by method of		
	Exp. V_b	Ref.	Tyn and Calus	Schroeder	Le Bas
Methane	37.7	46	−6.7	−7.2	−21.5
Propane	74.5	104	0.2	3.3	−0.7
Heptane	162	46	1.8	−0.6	0.5
Cyclohexane	117	46	−1.2	1.7	1.0
Ethylene	49.4	46	−6.0	−0.8	−10
Benzene	96.5	46	−0.1	1.6	−0.5
Fluorobenzene	102	46	−0.9	−0.5	−1.0
Bromobenzene	120	46	1.6	2.1	−1.6
Chlorobenzene	115	46	0.0	0.0	1.7
Iodobenzene	130	46	1.9	−0.4	−0.5
Methanol	42.5	46	−0.5	−1.2	−13
n-Propyl alcohol	81.8	46	−1.4	2.7	−0.5
Dimethyl ether	63.8	46	2.0	−1.3	−4.5
Ethyl propyl ether	129	46		−2.3	−0.5
Acetone	77.5	46	−0.6	−0.6	−4.5
Acetic acid	64.1	46	−2.7	−1.7	6.7
Isobutyric acid	109	46	0.3	−3.7	3.5
Methyl formate	62.8	46	0.0	0.3	−0.3
Ethyl acetate	106	46	0.9	−0.9	2.5
Diethylamine	109	46	3.5	2.8	2.7
Acetonitrile	57.4	46	10	−2.4	
Methyl chloride	50.6	46	−0.8	3.7	−0.2
Carbon tetrachloride	102	46	1.0	2.8	11
Diochlorodifluoromethane	80.7	42	−0.8	−4.6	0.9
Ethyl mercaptan	75.5	46	0.9	2.0	2.5
Diethyl sulfide	118	46	1.3	0.9	3.2
Phosgene	69.5	46	0.2	0.7	2.7
Ammonia	25.0	46	1.5	12	
Chlorine	45.5	46	−2.1	7.7	8.1
Water	18.7	45	3.5	12	
Hydrochloric acid	30.6	46	−6.8	2.9	−7.5
Sulfur dioxide	43.8	103	0.0	−12	−3.7
Average error			1.9	3.1	3.9

†Percent error = [calc. − exp.)/exp.] × 100

where both V_b and V_c are expressed in cubic centimeters per mole. This simple relation is generally accurate within 3 percent except for the low-boiling permanent gases (He, H_2, Ne, Ar, Kr) and some polar nitrogen and phosphorus compounds (HCN, PH_3). A similar relation was suggested earlier by Benson [8], but in that case the critical pressure also was employed in the correlation.

Recommendation

The Tyn and Calus method is recommended for estimating liquid molar volumes at the boiling point. The average error for 32 compounds is only 2 percent, as shown in Table 3-9. A reliable value of the critical volume must be available, however.

Example 3-4 Estimate the molar volume of liquid chlorobenzene at its normal boiling point. The critical volume is 308 cm³/mol (Appendix A). The experimental value is 115 cm³/mol.

solution SCHROEDER METHOD. From Table 3-8, C = 7, H = 7, Cl = 24.5, the ring = −7, and each double bond = 7. Therefore, for C_6H_5Cl

$$V_b = (6)(7) + (5)(7) + 24.5 - 7 + (3)(7) = 115 \text{ cm}^3/\text{mol}$$

$$\text{Error} = \frac{115 - 115}{115} \times 100 = 0\%$$

LE BAS METHOD. From Table 3-8, C = 14.8, H = 3.7, Cl = 24.6, and the ring = −15.0. Therefore,

$$V_b = (6)(14.8) + (5)(3.7) + 24.6 - 15.0 = 117 \text{ cm}^3/\text{mol}$$

$$\text{Error} = \frac{117 - 115}{115} \times 100 = +1.7\%$$

TYN AND CALUS METHOD. With Eq. (3-10.1),

$$V_b = 0.285 V_c^{1.048} = (0.285)(308^{1.048}) = 115 \text{ cm}^3/\text{mol}$$

$$\text{Error} = \frac{115 - 115}{115} \times 100 = 0\%$$

3-11   Estimation of Liquid Densities

Even if no data are available, there are a number of techniques for estimating pure liquid specific volumes or densities. Three techniques are presented to estimate *saturated* liquid densities; one is presented for compressed liquids.

Hankinson-Brobst-Thomson (HBT) technique

Hankinson and Thomson [33] present the following correlation for saturated densities of liquids:

$$\frac{V_s}{V^*} = V_R^{(0)} [1 - \omega_{SRK} V_R^{(\delta)}] \tag{3-11.1}$$

$$V_R^{(0)} = 1 + a(1 - T_r)^{1/3} + b(1 - T_r)^{2/3} + c(1 - T_r) + \tag{3-11.2}$$

$$d(1 - T_r)^{4/3} \qquad 0.25 < T_r < 0.95$$

$$V_R^{(\delta)} = [e + f T_r + g T_r^2 + h T_r^3]/(T_r - 1.00001) \tag{3-11.3}$$

$$0.25 < T_r < 1.0$$

When computing T_r, T_c should be obtained from Table 3-10. Values of the constants are:

a	-1.52816	b	1.43907
c	-0.81446	d	0.190454
e	-0.296123	f	0.386914
g	-0.0427258	h	-0.0480645

V^* is a pure component characteristic volume generally within 1 to 4 percent of the critical volume; ω_{SRK} is the acentric factor which forces the Soave equation to give a best fit of existing vapor pressure data. Values of V^* and ω_{SRK} for over 400 compounds given in Refs. 33, 71, and 102 are listed in Table 3-10.

If a value of V^* is not available, it may be estimated by:

$$V^* = \frac{RT_c}{P_c}(a + b\omega_{SRK} + c\omega_{SRK}^2) \tag{3-11.4}$$

Values for the constants in Eq. (3-11.4) are given in the accompanying tables.

Constant	Paraffins	Olefins and diolefins	Cycloparaffins	Aromatics	All hydrocarbons
a	0.2905331	0.3070619	0.6564296	0.2717636	0.2851686
b	-0.08057958	-0.2368581	-3.391715	-0.05759377	-0.06379110
c	0.02276965	0.2834693	7.442388	0.05527757	0.01379173
Avg. abs. % error in V_s	1.23%	1.43%	1.00%	0.58%	1.89%

Constant	Sulfur compounds	Fluorocarbons	Cryogenic liquids	Condensable gases
a	0.3053426	0.5218098	0.2960998	0.2828447
b	-0.1703247	-2.346916	-0.05468500	-0.1183987
c	0.1753972	5.407302	-0.1901563	0.1050570
Avg. abs. % error in V_s	1.98%	0.82%	0.85%	3.65%

If no data are available for a compound, ω_{SRK} should be replaced by the true acentric factor. The change in V_s will often be less than 1 percent but can be as high as 4 percent. If a compound does not fit into the categories described for Eq. (3-11.4), V^* may be replaced by the true critical volume. Again the resulting error will often be less than 1 percent but can be as high as 4 percent. The temperature-dependent criticals suggested by Gunn et al. [28] were used for hydrogen and helium.

TABLE 3-10 Pure Component Parameters for the Hankinson-Brobst-Thomson and the Rackett Liquid Volume Correlations† [33, 71, 102]

Paraffins	T_c, K‡	ω_{SRK}	V^*, L/mol	Z_{RA}
Methane	190.58	0.0074	0.0994	0.2892
Ethane	305.42	0.0983	0.1458	0.2808
Propane	369.82	0.1532	0.2001	0.2766
n-Butane	425.18	0.2008	0.2544	0.2730
Isobutane	408.14	0.1825	0.2568	0.2754
n-Pentane	469.65	0.2522	0.3113	0.2684
Isopentane	460.43	0.2400	0.3096	0.2717
Neopentane	433.78	0.1975	0.3126	0.2756
n-Hexane	507.43	0.3007	0.3682	0.2635
2-Methylpentane	497.50	0.2791	0.3677	0.2672
3-Methylpentane	504.43	0.2741	0.3633	0.2690
2,2-Dimethylbutane	488.78	0.2330	0.3634	0.2733
2,3-Dimethylbutane	499.98	0.2477	0.3610	0.2705
n-Heptane	540.26	0.3507	0.4304	0.2604
2,2-Dimethylpentane	520.50	0.2882	0.4225	0.2684
2,4-Dimethylpentane	519.79	0.3040	0.4251	0.2671
3,3-Dimethylpentane	536.40	0.2681	0.4137	0.2707
2,3-Dimethylpentane	537.35	0.2973	0.4127	0.2703
2-Methylhexane	530.37	0.3310	0.4274	0.2638
3-Methylhexane	535.25	0.3243	0.4231	0.2654
3-Ethylpentane	540.64	0.3118	0.4163	0.2658
2,2,3-Trimethylbutane	531.17	0.2511	0.4125	0.2727
n-Octane	568.83	0.3998	0.4904	0.2571
Isooctane	543.96	0.3045	0.4790	0.2684
2,2,3,3-Tetramethylbutane	567.93	0.2513	0.4569	0.2738
2-Methylheptane	559.57	0.3780	0.4889	
3-Methylheptane	563.60	0.3699	0.4837	
4-Methylheptane	561.67	0.3708	0.4841	
2,2-Dimethylhexane	549.80	0.3374	0.4829	
2,3-Dimethylhexane	563.42	0.3458	0.4765	
2,4-Dimethylhexane	553.45	0.3425	0.4811	
2,5-Dimethylhexane	549.99	0.3556	0.4858	
3,4-Dimethylhexane	568.78	0.3376	0.4722	
2,2,3-Trimethylpentane	563.43	0.2965	0.4679	
2,3,3-Trimethylpentane	573.49	0.2889	0.4632	
2,3,4-Trimethylpentane	566.34	0.3144	0.4689	
n-Nonane	594.64	0.4478	0.5529	0.2543
2-Methyloctane	586.60	0.4225	0.5524	
2,3-Dimethylheptane	589.60	0.3848	0.5383	
2,6-Dimethylheptane	577.90	0.4006	0.5500	
3-Ethylheptane	590.40	0.4083	0.5415	
2,2,3-Trimethylhexane	588.00	0.3349	0.5283	
2,2,4-Trimethylhexane	573.70	0.3481	0.5361	
2,2,5-Trimethylhexane	568.00	0.3569	0.5408	
2,2,3,4-Tetramethylpentane	592.70	0.3122	0.5198	
2,3,3,4-Tetramethylpentane	607.60	0.3117	0.5127	
3,3-Diethylpentane	610.00	0.3365	0.5175	
n-Decane	617.65	0.4916	0.6192	0.2507
4-Methylnonane	610.50	0.4572	0.6104	
2,7-Dimethyloctane	602.90	0.4432	0.6135	
3,3,5-Trimethylheptane	609.60	0.3827	0.5895	

TABLE 3-10 Pure Component Parameters for the Hankinson-Brobst-Thomson and the Rackett Liquid Volume Correlations† [33, 71, 102] (*Continued*)

Paraffins	T_c, K‡	ω_{SRK}	V^*, L/mol	Z_{RA}
2,2,3,3,-Tetramethylhexane	623.10	0.3646	0.5737	
2,2,5,5-Tetramethylhexane	581.50	0.3760	0.5992	
n-Undecane	638.73	0.5422	0.6865	0.2499
n-Dodecane	658.26	0.5807	0.7558	0.2466
n-Tridecane	675.76	0.6340	0.8317	0.2473
n-Tetradecane	691.87	0.6821	0.9022	
n-Pentadecane	706.76	0.7254	0.9772	
n-Hexadecane	720.54	0.7667	1.0539	0.2388
n-Heptadecane	733.37	0.7946	1.1208	0.2343
n-Octadecane	745.26	0.8124	1.1989	0.2275
n-Nonadecane	755.93	0.8328	1.2715	0.2236
n-Eicosane	767.04	0.9239	1.3754	0.2281
Heneicosane	776.77	1.0505	1.5081	0.2363
Docosane	788.99	1.0561	1.5839	0.2350
Tricosane	801.29	1.0477	1.6507	0.2341
Tetracosane	813.65	1.0316	1.7104	
Pentacosane	826.24	1.0014	1.7887	
Hexacosane	839.30	0.9498	1.8133	0.2302
Heptacosane	852.66	0.9001	1.9420	
Octacosane	866.44	0.8455	1.8972	0.2277
Triacontane	840.35	0.9919	2.0455	
Dotriacontane	850.57	1.0045	2.2453	
Tetracontane	882.18	0.9781	2.7094	
Tritetracontane	891.12	0.9214	2.9342	

Halogenated Paraffins				
Fluoromethane (R-41)	317.70	0.1851	0.1054	0.2491
Chloromethane (R-40)	416.25	0.1472	0.1363	0.2679
Bromomethane	464.00	0.2032	0.1506	
Nitromethane	588.00	0.3295	0.1626	
Dichloromethane (R-30)	510.00	0.1959	0.1767	0.2618
Chloroform (R-20)	536.40	0.2181	0.2245	0.2750
Trifluorobromomethane (R-13B1)	340.20	0.1700	0.1970	
Carbon tetrachloride (R-10)	556.40	0.1875	0.2754	0.2722
Trichlorofluoromethane (R-11)	471.15	0.1871	0.2460	0.2745
Dichlorodifluoromethane (R-12)	385.15	0.1699	0.2147	0.2757
Chlorotrifluoromethane (R-13)	302.00	0.1747	0.1807	0.2771
Dichloromonofluoromethane (R-21)	451.65	0.2102	0.1958	0.2705
Monochlorodifluoromethane (R-22)	369.15	0.2215	0.1637	0.2663
Trichlorotrifluoroethane (R-113)	487.26	0.2560	0.3263	0.2721
Dichlorotetrafluoroethane (R-114)	418.87	0.2582	0.2954	0.2737
Fluoroethane	375.31	0.2150	0.1577	
Chloroethane (R-160)	460.40	0.1880	0.1858	0.2654
Bromoethane	503.80	0.2266	0.2064	0.2896
1,1-Dichloroethane (R-150A)	523.00	0.2365	0.2369	
1,2-Dichloroethane	561.00	0.2754	0.2302	
2-Fluoropropane	417.26	0.1822	0.2130	
1-Chloropropane	503.00	0.2263	0.2434	
2-Chloropropane	485.00	0.2474	0.2494	
1,2,3-Trichloropropane	651.00	0.3282	0.3279	
1-Chlorobutane	542.00	0.2265	0.2969	

	T_c, K‡	ω_{SRK}	V^*, L/mol	Z_{RA}
Halogenated Paraffins (*Continued*)				
2-Chlorobutane	520.60	0.2920	0.3019	
tert-Butyl chloride	507.00	0.1999	0.3031	
Cycloparaffins				
Cyclopropane	397.81	0.1305	0.1610	0.2716
Cyclopentane	511.76	0.1969	0.2600	0.2745
Methylcyclopentane	532.79	0.2322	0.3181	0.2711
Cyclohexane	553.54	0.2128	0.3090	0.2729
Methylcyclohexane	572.19	0.2371	0.3709	0.2704
1,1-Dimethylcyclopentane	547.04	0.2691	0.3754	0.2768
1-*trans*-3-Dimethylcyclopentane	553.15	0.2676	0.3796	0.2768
1-*trans*-2-Dimethylcyclopentane	553.15	0.2689	0.3784	0.2763
1-*cis*-3-Dimethylcyclopentane	550.93	0.2825	0.3825	0.2823
1-*cis*-2-Dimethylcyclopentane	564.82	0.2685	0.3706	0.2699
Ethylcyclopentane	569.46	0.2689	0.3740	
1,1,2-Trimethylcyclopentane	579.50	0.2527	0.4255	
1,1,3-Trimethylcyclopentane	569.50	0.2173	0.4330	
1,1-Dimethylcyclohexane	591.00	0.2351	0.4216	
trans-1,3-Dimethylcyclohexane	598.00	0.2374	0.4213	
trans-1,4-Dimethylcyclohexane	590.00	0.2395	0.4319	
Ethylcyclohexane	609.00	0.2497	0.4227	
Propylcyclohexane	639.00	0.2654	0.4812	
Cyclodecane	709.00	0.2803	0.5100	
1,2-Dicyclohexylethane	756.92	0.4986	0.7482	
Olefins				
Ethylene	282.36	0.0882	0.1310	0.2815
Propylene	364.76	0.1455	0.1829	0.2779
1-Butene	419.59	0.1921	0.2377	0.2736
cis-2-Butene	435.58	0.2039	0.2311	0.2701
trans-2-Butene	428.63	0.2153	0.2367	0.2720
Isobutene	417.90	0.1959	0.2369	0.2728
1-Pentene	464.78	0.2824	0.2951	0.2899
cis-2-Pentene	475.93	0.2426	0.2875	0.2671
trans-2-Pentene	475.37	0.2399	0.2929	0.2704
2-Methyl-1-Butene	465.37	0.2355	0.2887	0.2627
3-Methyl-1-Butene	450.37	0.2266	0.2940	0.2739
2-Methyl-2-Butene	470.37	0.2852	0.2883	0.2592
1-Hexene	504.03	0.2850	0.3509	0.2658
cis-2-Hexene	518.00	0.2509	0.3447	
trans-3-Hexene	516.00	0.2532	0.3491	
cis-3-Hexene	517.00	0.2318	0.3465	
trans-3-Hexene	519.00	0.2153	0.3473	
2,3-Dimethyl-1-Butene	501.00	0.2242	0.3425	
3,3,-Dimethyl-1-Butene	490.00	0.1499	0.3466	
2-Ethyl-1-Butene	515.46	0.2100	0.3395	
2-Methyl-1-Pentene	511.54	0.2099	0.3433	
1-Heptene	533.29	0.3639	0.4113	0.2611
2,3,3-Trimethyl-1-Butene	533.00	0.1981	0.3914	
2,3-Dimethyl-1-Pentene	537.57	0.2318	0.3955	
1-Octene	566.65	0.3876	0.4710	0.2600

TABLE 3-10 Pure Component Parameters for the Hankinson-Brobst-Thomson and the Rackett Liquid Volume Correlations† [33, 71, 102] (*Continued*)

	T_c, K‡	ω_{SRK}	V^*, L/mol	Z_{RA}
Olefins (*Continued*)				
trans-2-Octene	580.00	0.3431	0.4674	
2,3-Dimethyl-2-hexene	577.15	0.3256	0.4510	
2,4,4-Trimethyl-1-pentene	560.15	0.2207	0.4510	
2,4,4-Trimethyl-2-pentene	563.15	0.2363	0.4493	
1-Nonene	592.04	0.4327	0.5333	0.2539
1-Decene	614.82	0.4975	0.6013	0.2546
1-Dodecene	657.00	0.5638	0.7340	
Halogenated Olefin				
Vinyl chloride (R-1140)	429.70	0.1293	0.1722	
Diolefins				
Propadiene	393.15	0.1430	0.1470	0.2584
1,2-Butadiene	443.71	0.2492	0.2183	0.2675
1,3-Butadiene	425.37	0.1934	0.2202	0.2712
1,2-Pentadiene	503.15	0.1760	0.2692	0.2677
cis-1,3-Pentadiene	499.15	0.1849	0.2691	
trans-1,3-Pentadiene	496.00	0.1830	0.2742	
Isoprene	484.26	0.1700	0.2691	0.2652
1,5-Hexadiene	507.00	0.2444	0.3306	
Cyclic Olefins				
Cyclopentene	506.00	0.1007	0.2375	
Cyclohexene	560.41	0.2091	0.2903	
4-Vinylcyclohexene	604.03	0.2883	0.3902	
1,5-Cyclooctadiene	647.23	0.2672	0.3717	
Acetylenes				
Acetylene	308.32	0.2049	0.1128	0.2709
Methylacetylene	402.39	0.2184	0.1609	0.2706
Vinyl acetylene	455.00	0.1335	0.1961	
Dimethylacetylene	488.15	0.1581	0.2106	0.2693
1-Butyne	463.71	0.0986	0.2154	0.2711
Aromatics				
Benzene	562.16	0.2137	0.2564	0.2698
Toluene	591.79	0.2651	0.3137	0.2644
o-Xylene	630.37	0.3118	0.3673	0.2620
m-Xylene	617.05	0.3270	0.3731	0.2625
p-Xylene	616.26	0.3216	0.3740	0.2592
1,2,3-Trimethylbenzene	664.45	0.3642	0.4183	
1,2,4-Trimethylbenzene	649.17	0.3745	0.4279	
1,3,5-Trimethylbenzene	637.28	0.3974	0.4337	
Ethylbenzene	617.17	0.3048	0.3702	
n-Propylbenzene	638.30	0.3432	0.4298	0.2599

	T_c, K‡	ω_{SRK}	V^*, L/mol	Z_{RA}
	Aromatics (*Continued*)			
Styrene	647.59	0.2420	0.3482	0.2634
Cumene	631.15	0.3277	0.4271	0.2617
n-Butylbenzene	660.40	0.3921	0.4921	
Isobutylbenzene	650.00	0.3921	0.4944	
sec-Butylbenzene	664.00	0.2817	0.4778	
tert-Butylbenzene	660.00	0.2710	0.4733	
Pentylbenzene	679.93	0.4406	0.5561	0.2547
Heptylbenzene	713.54	0.5441	0.6906	0.2508
Nonylbenzene	740.93	0.6583	0.8369	0.2471
Undecylbenzene	764.26	0.7659	0.9919	0.2444
Tridecylbenzene	783.15	0.9001	1.1693	0.2434
Heptadecylbenzene	818.76	0.9404	1.4564	
Tricosylbenzene	847.43	1.1399	1.9952	
Heavy aromatic	895.75	0.7619	2.2323	
Naphthalene	748.35	0.3000	0.3834	
1-Methylnaphthalene	772.00	0.3422	0.4504	
2-Methylnaphthalene	761.00	0.3669	0.4591	
Tetralin	719.00	0.3209	0.4304	
Biphenyl	789.00	0.3633	0.4890	0.2743
Phenanthrene	878.00	0.4316	0.5711	
	Aromatic Derivatives			
Fluorobenzene	560.09	0.2434	0.2702	0.2662
Chlorobenzene	632.40	0.2461	0.3056	0.2651
Bromobenzene	670.00	0.2481	0.3204	0.2637
Nitrobenzene	718.86	0.4348	0.3339	
Iodobenzene				0.2645
	Heterocycles			
Ethylene oxide	468.15	0.2114	0.1345	0.2569
1,2-Propylene oxide	482.20	0.2593	0.1910	
Furan	490.25	0.2061	0.1968	
Tetrahydrofuran	540.15	0.2227	0.2308	
Pyrrole	640.00	0.3305	0.2130	
Pyrrolidine	568.55	0.2718	0.2423	
n-Methylpyrrolidone	723.59	0.3654	0.3070	
Thiophene	579.40	0.1934	0.2279	
Thiophane	622.15	0.2299	0.2626	
Sulfolane	854.88	0.3591	0.3136	0.2384
3-Methyl sulfolane	817.38	0.4132	0.4127	
1,4-Dioxane	587.00	0.2779	0.2523	
Pyridine	620.00	0.2398	0.2400	
	Nitriles			
Acetonitrile	548.00	0.3076	0.1606	0.1987
Acrylonitrile	536.00	0.3369	0.1918	0.2275
Benzonitrile	699.40	0.3566	0.3257	

TABLE 3-10 Pure Component Parameters for the Hankinson-Brobst-Thomson and the Rackett Liquid Volume Correlations† [33, 71, 102] (*Continued*)

	T_c, K‡	ω_{SRK}	V^*, L/mol	Z_{RA}
Acids and Anhydrides				
Hydrogen cyanide	456.80	0.3838	0.1076	
Formic acid	580.00	0.4700	0.1170	0.1880
Acetic acid	594.45	0.4310	0.1741	0.2225
Trifluoroacetic acid	491.30	0.5335	0.2285	
Adipic acid	809.11	1.1045	0.4844	
Stearic acid	798.83	1.2312	1.3430	
Acetic anhydride	569.00	0.9057	0.3287	
Esters				
Methyl acetate	506.80	0.3205	0.2262	0.2552
Ethyl acetate	523.20	0.3595	0.2853	0.2539
Vinyl acetate	525.00	0.3362	0.2669	0.2573
Methyl acrylate	536.00	0.3373	0.2640	
Ethyl acrylate	552.00	0.3908	0.3245	
Methyl methacrylate	563.15	0.2890	0.3112	
Amides				
Formamide	765.33	0.4061	0.1305	
n-Methylformamide	727.30	0.3965	0.1893	
n,n-Dimethylformamide	643.15	0.3672	0.2399	
Acetamide	760.79	0.4292	0.1830	
Propionamide	730.31	0.4559	0.2406	
Aldehydes				
Formaldehyde	408.00	0.2656	0.1001	
Acetaldehyde	460.93	0.2647	0.1519	0.2269
Furfural	670.15	0.3847	0.2622	
Ketones				
Ketene	380.00	0.0967	0.1450	
Acetone	508.15	0.3149	0.2080	0.2477
Methyl ethyl ketone	536.78	0.3188	0.2523	
Diethyl ketone	561.00	0.3465	0.3034	
Methyl isopropyl ketone	553.00	0.3323	0.3156	
Methyl isobutyl ketone	571.00	0.3743	0.3758	
Cyclopentanone	626.00	0.2949	0.2686	
Cyclohexanone	629.00	0.4409	0.3271	0.2465
Alcohols				
Methanol	513.15	0.5536	0.1198	0.2334
Ethanol	516.16	0.6378	0.1752	0.2502
1-Propanol	537.04	0.6249	0.2305	0.2541
Isopropanol	508.76	0.6637	0.2313	0.2493
1-Butanol	562.93	0.5928	0.2841	0.2538
Isobutanol	547.73	0.5883	0.2730	
sec-Butanol	535.95	0.5792	0.2803	

	T_c, K‡	ω_{SRK}	V^*, L/mol	Z_{RA}
Alcohols (*Continued*)				
tert-Butanol	506.20	0.6134	0.2876	
1-Pentanol	586.00	0.5975	0.3437	0.2596
2-Methyl-1-butanol	571.00	0.6108	0.3407	
3-methyl-1-butanol	579.40	0.5629	0.3413	
2-methyl-2-butanol	545.00	0.5007	0.3313	
3-Pentanol	542.62	0.7094	0.3434	
1-Dodecanol	679.00	1.1256	0.8283	
Allyl alcohol	508.31	0.6663	0.2273	
Furfuryl alcohol	597.30	0.5887	0.4900	
Cyclohexanol	625.00	0.5296	0.3377	
Benzyl alcohol	677.00	0.7231	0.3591	
Glycols				
Ethylene glycol	647.15	1.2280	0.2120	0.2488
Diethylene glycol	680.15	1.0713	0.3522	0.2489
Triethylene glycol	710.15	1.2540	0.5347	0.2462
Tetraethylene glycol	747.59	1.7224	0.8966	
Glycerol	726.00	1.9845	0.4119	
Phenol				
Phenol	694.20	0.4297	0.2809	0.2780
Amines				
Methyl amine	430.70	0.2872	0.1223	
Dimethyl amine	437.22	0.3044	0.1812	
Ethyl amine	456.00	0.2871	0.1772	0.2642
Diethyl amine	496.60	0.3045	0.2906	0.2568
Triethyl amine	535.00	0.3196	0.4026	0.2693
Hexamethylene diamine	666.53	0.6418	0.4260	
Aniline	699.00	0.3809	0.2901	0.2616
Monoethanolamine	636.76	0.8271	0.2135	
Diethanolamine	706.54	1.5299	0.4543	0.2527
Diisopropanol amine	672.35	1.4690	0.6151	
Ethers				
Dimethyl ether	400.00	0.1972	0.1692	0.2742
Ethyl ether	466.76	0.2800	0.2812	0.2632
Methyl ethyl ether	437.80	0.2401	0.2216	0.2673
Methyl *n*-butyl ether	512.78	0.3137	0.3372	
Methyl isobutyl ether	496.31	0.3049	0.3379	
Methyl *tert*-butyl ether	497.10	0.2670	0.3249	
Diisopropyl ether	500.32	0.3300	0.3995	
Methyl vinyl ether	436.00	0.2489	0.2011	
Ethyl vinyl ether	475.00	0.2673	0.2477	
Mercaptans				
Methyl mercaptan	469.93	0.1567	0.1508	0.2781
Ethyl mercaptan	499.26	0.1915	0.2023	0.2704

TABLE 3-10 Pure Component Parameters for the Hankinson-Brobst-Thomson and the Rackett Liquid Volume Correlations† [33, 71, 102] (*Continued*)

	T_c, K‡	ω_{SRK}	V^*, L/mol	Z_{RA}
Mercaptans (*Continued*)				
n-Propyl mercaptan	535.64	0.2380	0.2572	0.2685
Isopropyl mercaptan	517.41	0.2105	0.2606	0.2810
n-Butyl mercaptan	569.11	0.2781	0.3135	0.2644
sec-Butyl mercaptan	554.01	0.2494	0.3139	0.2731
Isobutyl mercaptan	559.44	0.2496	0.3159	0.2725
tert-Butyl mercaptan	530.14	0.1966	0.3162	0.2831
n-amyl mercaptan	597.79	0.3235	0.3728	0.2613
2-Pentanethiol	581.90	0.2932	0.3709	0.2685
3-Pentanethiol	584.17	0.2931	0.3676	0.2666
Isoamyl mercaptan	591.88	0.2935	0.3663	0.2641
3-Methyl-1-butanethiol	590.89	0.2934	0.3697	0.2658
tert-amyl mercaptan	570.13	0.2390	0.3674	0.2722
sec-Isoamyl mercaptan	583.53	0.2641	0.3650	0.2698
tert-Butyl methyl mercaptan	577.10	0.2393	0.3661	
n-Hexyl mercaptan	622.73	0.3726	0.4335	0.2583
sec-Hexyl mercaptan	607.84	0.3413	0.4310	0.2646
tert-Hexyl mercaptan	595.39	0.2861	0.4233	
Diisopropyl mercaptan	602.64	0.2562	0.4160	0.2664
n-Heptyl mercaptan	644.82	0.4253	0.4971	0.2557
sec-Heptyl mercaptan	630.80	0.3932	0.4939	0.2614
n-Octyl mercaptan	663.77	0.4808	0.5616	0.2532
sec-Octyl mercaptan	650.80	0.4477	0.5579	0.2583
n-Nonyl mercaptan	680.86	0.5388	0.6301	0.2514
sec-Nonyl mercaptan	669.47	0.5048	0.6258	0.2559
n-Decyl mercaptan	696.37	0.5986	0.7007	0.2493
sec-Decyl mercaptan	685.81	0.5640	0.6957	0.2534
Benzenethiol	689.52	0.2677	0.3157	
Benzyl mercaptan	710.17	0.3101	0.3704	
Sulfides				
Carbonyl sulfide	375.37	0.1021	0.1410	0.2709
Dimethyl sulfide	503.04	0.1936	0.2010	0.2692
Methyl ethyl sulfide	533.15	0.2435	0.2569	0.2689
Methyl n-propyl sulfide	564.82	0.2770	0.3129	0.2653
Diethyl sulfide	557.04	0.2938	0.3137	0.2671
Methyl isopropyl sulfide	553.71	0.2494	0.3133	0.2728
Methyl n-butyl sulfide	593.15	0.3220	0.3716	0.2620
Ethyl n-propyl sulfide	585.37	0.3250	0.3728	0.2643
Methyl sec-butyl sulfide	581.48	0.2946	0.3715	0.2688
Methyl isobutyl sulfide	582.04	0.2933	0.3705	0.2683
Ethyl isopropyl sulfide	574.26	0.2940	0.3730	0.2713
Methyl tert-butyl sulfide	569.82	0.2387	0.3666	0.2720
Ethyl n-butyl sulfide	610.37	0.3730	0.4355	0.2611
Di-n-propyl sulfide	608.15	0.3741	0.4332	0.2615
n-Propyl isopropyl sulfide	597.59	0.3428	0.4328	0.2677
Ethyl sec-butyl sulfide	600.37	0.3398	0.4288	0.2658
Ethyl isobutyl sulfide	600.93	0.3421	0.4316	0.2665
Ethyl tert-butyl sulfide	588.71	0.2848	0.4276	0.2704
Diisopropyl sulfide	585.37	0.3098	0.4327	0.2747

	T_c, K‡	ω_{SRK}	V^*, L/mol	Z_{RA}
Sulfides (*Continued*)				
Di-*n*-butyl sulfide	649.26	0.4824	0.5616	0.2561
Diisoamyl sulfide	664.26	0.6181	0.7013	0.2589
Diallyl sulfide	653.15	0.1031	0.3732	0.2525
Disulfides				
Dimethyl disulfide	605.74	0.2610	0.2638	0.2751
Diethyl disulfide	642.04	0.3424	0.3803	0.2694
Ethyl *n*-propyl disulfide	657.07	0.3876	0.4403	0.2662
Ethyl isopropyl disulfide	650.71	0.3556	0.4392	0.2711
Di-*n*-propyl disulfide	675.31	0.4391	0.5041	0.2634
Propyl isopropyl disulfide	666.40	0.4059	0.5023	0.2680
Ethyl *tert*-butyl disulfide	659.92	0.3482	0.4950	0.2696
Diisopropyl disulfide	659.36	0.3734	0.4999	0.2727
Di-*n*-butyl disulfide	699.64	0.5507	0.6359	0.2589
Di-*tert*-butyl disulfide	691.68	0.2939	0.4933	
Di-*n*-amyl disulfide	721.73	0.6707	0.7803	0.2552
Di-*n*-hexyl disulfide	741.59	0.7928	0.9399	0.2525
Di-*tert*-dodecyl disulfide	728.14	1.0299	1.7258	
Inorganic Gases				
Hydrogen	33.15	− 0.2324	0.0642	0.3060
Oxygen	154.09	0.0298	0.0738	0.2905
Nitrogen	126.25	0.0358	0.0901	0.2900
Air	132.41	− 0.0031	0.0875	0.2692
Carbon monoxide	133.15	0.0295	0.0921	0.2896
Carbon dioxide	304.15	0.2373	0.0938	0.2722
Fluorine	144.30	0.0493	0.0669	0.2887
Chlorine	417.11	0.0822	0.1223	0.2767
Hydrogen fluoride	461.00	0.3281	0.0586	0.1451
Hydrogen chloride	324.54	0.1254	0.0838	0.2653
Hydrogen bromide	363.20	0.0779	0.0992	
Sulfur dioxide	430.59	0.2645	0.1204	0.2661
Sulfur trioxide	491.37	0.5025	0.1222	0.2515
Hydrogen sulfide	373.65	0.0930	0.0994	0.2855
Carbon disulfide	552.04	0.1035	0.1690	0.2808
Ammonia	405.43	0.2620	0.0701	0.2465
Hydrazine	653.15	0.3410	0.0984	0.2640
Nitrous oxide	309.58	0.1691	0.0980	0.2758
Nitric oxide	180.37	0.5896	0.0665	0.2668
Nitrogen dioxide	431.37	0.8634	0.0912	0.2413
Nitrogen tetroxide	431.15	0.8573	0.1894	0.3665
Helium	5.37	− 0.4766	0.0546	0.2981
Neon	44.40	− 0.0362	0.0425	0.3085
Argon	150.80	− 0.0092	0.0754	0.2922
Krypton	209.40	− 0.0050	0.0917	0.2901
Xenon	289.73	− 0.0023	0.1135	0.2829
Oils and Petroleum Products				
Jet fuel naphtha (44.4 grav.)	622.18	0.3982	0.5083	
Aromatic naphtha (34.5 grav.)	593.46	0.3120	0.3522	

TABLE 3-10   Pure Component Parameters for the Hankinson-Brobst-Thomson and the Rackett Liquid Volume Correlations† [33, 71, 102] (*Continued*)

	T_c, K‡	ω_{SRK}	V^*, L/mol	Z_{RA}
Oils and Petroleum Products (*Continued*)				
Low-boiling naphtha (59.9 grav.)	571.39	0.3708	0.4686	
High-boiling naphtha (54.2 grav.)	608.31	0.4212	0.5562	
Kerosene (43.5 grav.)	664.30	0.4783	0.6674	
Fuel oil (33.0 grav.)	745.21	0.6009	0.9150	
Gas oil (35.3 grav.)	738.70	0.6007	0.9256	
Miscellaneous				
Water	647.37	0.3852	0.0436	0.2338
Sulfuric acid	899.79	0.9302	0.1230	
Dimethyl sulfoxide	727.56	0.2985	0.2288	
Di-*n*-propyl sulfone	763.52	0.5771	0.4937	
Di-*n*-butyl sulfone	766.74	0.6928	0.6302	
Dowtherm A	770.37	0.4084	0.5185	0.2542

†The Phillips Petroleum Company is gratefully acknowledged for providing many of the values in this table.

‡T_c values in many cases are not experimental values and should be used only in Eqs. (3-11.2) and (3-11.3). More reliable values of the true T_c are given in Appendix A.

More recently, Thomson et al. [119] have extended the HBT method to allow prediction of compressed liquid volumes by generalizing the constants in the Tait equation. Thus

$$V = V_s\left(1 - c \ln \frac{\beta + P}{\beta + P_{vp}}\right) \qquad (3\text{-}11.5)$$

V_s, the saturated liquid volume at the vapor pressure P_{vp}, should be obtained from Eq. (3-11.1). β and c are obtained from

$$\beta/P_c = -1 + a(1 - T_r)^{1/3} + b(1 - T_r)^{2/3} \\ + d(1 - T_r) + e(1 - T_r)^{4/3} \qquad (3\text{-}11.6)$$

where $e = \exp(f + g\omega_{SRK} + h\omega_{SRK}^2)$ (3-11.7)

and $c = j + k\omega_{SRK}$ (3-11.8)

Values of P_c should be obtained from Appendix A. The constants a through k for Eqs. (3-11.6) to (3-11.8) are:

a	-9.070217	b	62.45326
d	-135.1102	f	4.79594
g	0.250047	h	1.14188
j	0.0861488	k	0.0344483

Modified Rackett technique

An equation to estimate saturated volumes which was developed by Rackett [95] and later modified by Spencer and Danner [102] is

$$V_s = \frac{RT_c}{P_c} Z_{RA}^{[1 + (1-T_r)^{2/7}]} \tag{3-11.9}$$

Z_{RA} is a unique constant for each compound, and sample values are listed in Table 3-10. If a value of Z_{RA} is not available, it may be estimated by [133]:

$$Z_{RA} = 0.29056 - 0.08775\omega \tag{3-11.10}$$

If one experimental density is available at a reference temperature T^R, the recommended form of the Rackett equation is

$$V_s = V_s^R Z_{RA}^\phi \tag{3-11.11}$$
where $\phi = (1-T_r)^{2/7} - (1-T_r^R)^{2/7}$ $\tag{3-11.12}$

Note that Eq. (3-11.9) does not predict the correct volume at the critical point unless $Z_{RA} = Z_c$.

Bhirud's method

Bhirud [5] has presented the following corresponding states equation for the saturated liquid volume of normal (nonpolar) fluids

$$\ln \frac{P_c V_s}{RT} = \ln V^{(0)} + \omega \ln V^{(1)} \tag{3-11.13}$$

$$\ln V^{(0)} = 1.39644 - 24.076T_r + 102.615T_r^2 - 255.719T_r^3 + 355.805T_r^4$$
$$- 256.671T_r^5 + 75.1088T_r^6 \tag{3-11.14}$$

$$\ln V^{(1)} = 13.4412 - 135.7437T_r + 533.380T_r^2 - 1091.453T_r^3 + 1231.43T_r^4$$
$$- 728.227T_r^5 + 176.737T_r^6 \tag{3-11.15}$$

Above $T_r = 0.98$, values of $\ln V^{(0)}$ and $\ln V^{(1)}$ from tables in [5] should be used. Equation (3-11.13) gave an average percent deviation of 0.76 percent for 752 data points for hydrocarbons for reduced temperatures between 0.3 and 1.0 [5]. Bhirud [6] has extended his method to polar compounds, but the extension requires an experimental density.

Other methods that can be used to estimate saturated liquid densities include those of Gunn and Yamada [29] and Yen and Woods [135]. They were reviewed in the third edition of this book. Hankinson and Thomson [33] have reviewed shortcomings of the two methods. The methods of Yen and Woods [135] as well as those of Chueh and Prausnitz [11] and Lyck-

man, Eckert, and Prausnitz [52] can be used for compressed liquids. These methods are, however, more complicated than the HBT method [Eqs. (3-11.5) to (3-11.8)] and appear to be less accurate [119]. Campbell and Thodos [10] have presented a method for predicting saturated liquid densities for both polar and nonpolar substances. The method requires, as input parameters, critical properties, the normal boiling point, and, for polar compounds, the dipole moment. The method has not been tested for mixtures, but it appears to give pure component results with an accuracy equivalent to the Hankinson and modified Rackett methods. Ouyang [79] has presented a group contribution type method based on "contact volume." The method requires the melting temperature, the critical temperature, and one experimental density.

Recommendation

To estimate the molar volume of saturated liquids, use either the Hankinson or Rackett equation with parameters from Table 3-10. If parameters are not listed in Table 3-10, Z_{RA} may be estimated with Eq. (3-11.10). For the Hankinson parameters, ω_{SRK} may be replaced with ω and V^* may be estimated with Eq. (3-11.4) or replaced with V_c. If a single experimental density is available, V^* may be calculated directly or for the Rackett equation, Eq. (3-11.11) may be used. For compressed liquids, use the HBT method, Eq. (3-11.5).

Example 3-5 For isobutane at 310.93 K, calculate the volume of the saturated liquid and compressed liquid at 137.9 bar. Experimental values [98] are 108.2 and 102.7 cm³/mol, respectively.

solution From Table 3-10, $\omega_{SRK} = 0.1825$, $V^* = 256.8$, and $Z_{RA} = 0.2754$. $T_r = 0.762$. Using the Hankinson method, Eqs. (3-11.1) to (3-11.3) give $V_R^{(0)} = 0.4399$, $V_R^{(\delta)} = 0.1990$, $V_s = (0.4399)(256.8)[(1 - (0.1825)(0.1990)] = 108.9$ cm³/mol (error = 0.6%).
For the compressed liquid case, Eqs. (3-11.6) to (3-11.8) give

$$c = 0.09244$$
$$e = 131.58$$
$$\beta/P_c = 4.615$$
$$\beta = (4.615)(36.5) = 168.3 \text{ bar}$$

From Ref. 107, $P_{vp} = 4.958$ bar; Eq. (3-11.5) gives

$$V = (108.9)(1 - 0.09244 \left(\ln \frac{168.3 + 137.9}{168.3 + 4.958} \right) = 103.2 \text{ cm}^3/\text{mol} \qquad (\text{error} = 0.5\%)$$

For saturated liquid, the Rackett equation (3-11.9) gives

$$V_s = \frac{(83.14)(408.2)}{36.5} (0.2754)^{[1 + (1 - 0.762)^{2/7}]} = 108.9 \text{ cm}^3/\text{mol} \qquad (\text{error} = 0.6\%)$$

Notation

In many equations in this chapter, special constants are defined and usually denoted $a, b, \ldots, A, B, \ldots$ They are not defined in this notation; for they apply to the specific equation and do not occur elsewhere in the chapter.

A^*, B^*	dimensionless parameters for cubic equations of state, see Eqs. (3-6.3), (3-6.4)
B	second virial coefficient, cm^3/mol
C	third virial coefficient, Eq. (3-5.1), $(cm^3/mol)^2$
M	molecular weight
P	pressure; P_{vp}, vapor pressure; P_c, critical pressure; P_r, reduced pressure, P/P_c, bar
R	gas constant, see Table 3-1
T	absolute temperature; T_c, critical temperature; T_r, reduced temperature, T/T_c; T_b, normal boiling point at 1 atm, kelvins
V	molar volume; V_c, critical volume; V_r, reduced volume, V/V_c; V_b, at normal boiling point; V_{ri}, ideal reduced volume, $V/(RT_c/P_c)$; V_s, saturated liquid volume, cm^3/mol
$V_R^{(0)}, V_R^{(\delta)}$	functions of T_r for HBT correlations, Eqs. (3-11.2) and (3-11.3)
V^*, ω_{SRK}	parameters for HBT correlations, Eq. (3-11.1) and Table 3-10
Z	compressibility factor, PV/RT; Z_c, at the critical point; $Z^{(0)}$, simple fluid compressibility factor, Eq. (3-3.1) and Table 3-2; $Z^{(1)}$, deviation compressibility factor, Eq. (3-3.1) and Table 3-3; Z_{RA}, Rackett compressibility factor, Eq. (3-11.9)

GREEK

μ	dipole moment, debyes; μ_r, reduced dipole moment, see Eq. (3-5.8)
ρ	molar density; ρ_c, critical density; ρ_r, reduced density, ρ/ρ_c; ρ_b, at normal boiling point; ρ_s, saturated liquid density
ϕ	fugacity coefficient
ω	Pitzer acentric factor, see Sec. 2-3

SUPERSCRIPTS

R	reference fluid or reference state
L	liquid phase property
V	vapor phase property

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Chapter

4

Volumetric Properties
of Mixtures

4-1 Scope

In Chap. 3 we reviewed methods for calculating the PVT properties of gases and liquids. To extend the methods to mixtures, they must be modified to include the additional variable of composition. In essentially all cases, the inclusion is accomplished by averaging pure component constants to obtain constants which hopefully characterize the mixtures. Equations which do this are called mixing rules. Many algebraic relations have been suggested, although it can be shown (Sec. 4-2) that essentially all can be derived from a single general expression. One must keep in mind that the rules covered in this chapter are, with a single exception [Eq. (4-4.1)], essentially empirical and have resulted from many trials and comparisons of calculated mixture properties with experimental data. Our *treatment is to present first a general discussion and then follow with the* recommended mixing rules for all gas PVT estimation methods covered in Chap. 3. Rules applicable to liquid mixtures are covered in Sec. 4-9.

This chapter is concerned primarily with the volumetric properties of mixtures. But mixing rules are used in the estimation of many other properties as well. Thus mixing rules appear in Chaps. 5, 8, 9, 10, 11, and 12. In Chap. 5 we examine the thermodynamic properties of both pure components and mixtures; for the former, one may simply use the constants

given with each method outlined in Chap. 3. For the latter, the equation-of-state parameters must be determined separately for each mixture with a different composition. In Chap. 8, and in particular, in Sec. 8-12, equations of state are used to calculate vapor-liquid equilibria. In this application derivatives of the mixing rules with respect to composition must accurately represent the true behavior. In Chaps. 9 to 12, mixing rules are used in the estimation of transport properties and the surface tension of mixtures.

4-2 Mixing Rules—General Discussion

Typically a mixing rule expresses a mixture parameter Q_m in terms of composition and pure component parameters according to

$$Q_m = \sum_i \sum_j y_i y_j Q_{ij} \tag{4-2.1}$$

In Eq. (4-2.1), the mole fractions y_i and y_j may apply to a liquid or vapor phase. Q_{ii} and Q_{jj} involve properties of the pure compounds i and j. For example, Q_{ii} might be the critical temperature of pure i. The difficulty arises when interaction terms Q_{ij} are considered. Rules used to find Q_{ij} are called combining rules. If Q_{ij} is set equal to either the arithmetic average or geometric mean, the double summation in Eq. (4-2.1) reduces to a single summation.

For $$Q_{ij} = \frac{Q_{ii} + Q_{jj}}{2} \qquad Q_m = \sum_i y_i Q_i \tag{4-2.2}$$

For $$Q_{ij} = (Q_{ii} Q_{jj})^{1/2} \qquad Q_m = \left(\sum_i y_i Q_i^{1/2} \right)^2 \tag{4-2.3}$$

where Q_{ii} and Q_i are the same quantity. Equations (4-2.2) and (4-2.3) correspond to the two combining and mixing rules van der Waals originally proposed for his equation. To improve performance, it is customary to add binary interaction parameters k_{ij} to the expressions for Q_{ij}. One possibility would be

$$Q_{ij} = \frac{k_{ij}(Q_{ii} + Q_{jj})}{2} \tag{4-2.4}$$

Values of k_{ii} would be taken as unity and values of k_{ij} for all possible binary pairs would be determined by regressing experimental mixture data. Values of k_{ij} are more sensitive to derivative, or partial properties (such as fugacity coefficients), than to total properties (such as mixture molar volumes). For that reason, values of k_{ij} have most often been deter-

mined from VLE data, although Brulé and Starling [4] suggest multiproperty regression. k_{ij} is usually assumed to be independent of temperature, pressure, and composition. As defined in Eq. (4-2.4), one would hope for values of k_{ij} close to unity, which would suggest the original model was reasonable and only a small correction was necessary to give the best fit to data. Other ways in which k_{ij} and Q_{ij} could be defined include

$$Q_{ij} = k_{ij}(Q_{ii}Q_{jj})^{1/2} \qquad (k_{ii} = 1) \qquad (4\text{-}2.5)$$

$$Q_{ij} = \frac{(1 - k_{ij})(Q_{ii} + Q_{jj})}{2} \qquad (k_{ii} = 0) \qquad (4\text{-}2.6)$$

$$Q_{ij} = (1 - k_{ij})(Q_{ii}Q_{jj})^{1/2} \qquad (k_{ii} = 0) \qquad (4\text{-}2.7)$$

In Secs. 4-3 to 4-6, four different binary interaction parameters, k_{ij}, k_{ij}^*, $\bar{k}_{ij}$, and k'_{ij} are introduced. Four symbols are used to emphasize that these four quantities are not numerically the same. They are, however, related to each other so that it would, in theory, be possible to calculate any three of the interaction parameters from the fourth. In practice this is usually not done.

The theory of mixing rules is discussed elsewhere [21, 31, 48] and will not be dealt with to any extent here. However, it is worth noting that, more often than not, an arithmetic average is used for size parameters and a geometric mean is used for energy parameters.

4-3 Corresponding States: The Pseudocritical Method

To apply the corresponding states correlations in Secs. 3-2 and 3-3 to mixtures, one must determine appropriate scaling factors. For mixtures, these scaling factors are called *pseudocritical properties*. Values of pseudocritical properties are not the same as those of true critical properties, but Eqs. (3-6.5) and (3-6.6) are satisfied at the pseudocritical point. The assumption in applying corresponding states is that the *PVT* behavior of the *mixture* will be the same as that of a *pure component* whose critical temperature and pressure are equal to the pseudocritical temperature and pressure of the mixture.

For the pseudocritical temperature T_{cm} a simple mole fraction average method is usually satisfactory. This rule, often called Kay's rule [27], is

$$T_{cm} = \sum_j y_j T_{cj} \qquad (4\text{-}3.1)$$

Comparison of T_{cm} from Eq. (4-3.1) with values determined from other, more complicated rules shows that the differences are usually less than 2 percent if, for all components [48],

$$0.5 < \frac{T_{ci}}{T_{cj}} < 2 \quad \text{and} \quad 0.5 < \frac{P_{ci}}{P_{cj}} < 2$$

For the pseudocritical pressure, a simple mole fraction average of the pure component critical pressures is normally not satisfactory unless all components have similar critical pressures or critical volumes. The simplest rule which gives acceptable results is the modified Prausnitz and Gunn combination [44]

$$P_{c_m} = \frac{R \left(\sum_j y_j Z_{c_j} \right) T_{c_m}}{\sum_j y_j V_{c_j}} \tag{4-3.2}$$

The mixture acentric factor is usually given by [24]:

$$\omega_m = \sum_j y_j \omega_j \tag{4-3.3}$$

although Brulé et al. [5] use a different rule.

No binary (or higher) interaction parameters are included in Eqs. (4-3.1) to (4-3.3); thus these mixing rules cannot truly reflect mixture properties. Yet surprisingly good results are often obtained when these simple pseudomixture parameters are used in corresponding states calculations to determine mixture properties.

Less satisfactory results are found for mixtures of dissimilar components, especially if one or more of the components is polar or shows any tendency to associate into dimers, etc.

However, if one has available some experimental data for any of the possible binaries in the mixture, it is frequently worthwhile to use those data to modify the pseudocritical rules. Though many options are open, one which has often proved successful is to change Eq. (4-3.1) from a linear to a quadratic form:

$$T_{c_m} = \sum_i \sum_j y_i y_j T_{cij} \tag{4-3.4}$$

with $\quad T_{cii} = T_{ci} \quad$ and $\quad T_{cij} = k_{ij}^* \dfrac{T_{ci} + T_{cj}}{2} \tag{4-3.5}$

In some instances, it is assumed that $T_{cij} = (T_{ci} T_{cj})^{1/2} (1 - k_{ij})$. It is clear that k_{ij}^* and k_{ij} are not the same, although they are easily related to one another. Also, the arithmetic and geometric means are essentially the same unless critical temperatures i and j are greatly different.

From the available data, the best values of the binary constants k_{ij}^* are back-calculated by trial and error. If k_{ij}^* is assumed equal to unity, Eq. (4-3.4) reduces to Eq. (4-3.1). With k_{ij}^* values for all possible binary sets,

TABLE 4-1   Barner and Quinlan k_{ij}^* Values [2]

Component				Component		
i	j	k_{ij}^*		i	j	k_{ij}^*
Methane	Ethylene	1.01		n- or Isobutane	Isobutane	1.00
	Ethane	1.03			n-Pentane	1.00
	Propylene	1.06			Isopentane	1.00
	Propane	1.07			n-Hexane	1.02
	n-Butane	1.11			n-Heptane	1.03
	Isobutane	1.11			Cyclohexane	1.01
	n-Pentane	1.15		n- or Isopentane	Isopentane	1.00
	Isopentane	1.15			n-Hexane	1.00
	n-Hexane	1.19			n-Heptane	1.01
	n-Heptane	1.22			n-Octane	1.02
	Cyclohexane	1.16			Cyclohexane	1.00
	Naphthalene	1.23		n-Hexane	n-Heptane	1.00
Ethylene	Ethane	1.00			n-Octane	1.01
	Propylene	1.02			Toluene	0.98
	Propane	1.02		Cyclohexane	n-Heptane	1.00
	n-Butane	1.05			n-Octane	1.00
	Isobutane	1.05			Toluene	0.99
	n-Pentane	1.08		n-Heptane	n-Octane	1.01
	Isopentane	1.08		Nitrogen	Methane	0.97
	n-Hexane	1.11			Ethylene	1.01
	Cyclohexane	1.09			Ethane	1.02
	n-Heptane	1.13			n-Butane	1.13
	Benzene	1.07			1-Pentene	1.13
	Naphthalene	1.15			1-Hexene	1.25
Ethane	Propylene	1.01			n-Hexane	1.26
	Propane	1.01			n-Heptane	1.31
	n-Butane	1.03			n-Octane	1.34
	Isobutane	1.03		Argon	Oxygen	0.99
	n-Pentane	1.05			Nitrogen	0.99
	Isopentane	1.05		Carbon dioxide	Ethylene	0.94
	n-Hexane	1.08			Ethane	0.92
	n-Heptane	1.10			Propylene	0.93
	Cyclohexane	1.06			Propane	0.93
	Benzene	1.04			n-Butane	0.93
	Naphthalene	1.11			Naphthalene	1.07
Propylene	Propane	1.00		Hydrogen sulfide	Methane	0.93
	n-Butane	1.01			Ethane	0.92
	Isobutane	1.01			Propane	0.92
	n-Pentane	1.02			n-Pentane	0.96
	Isopentane	1.03			Carbon dioxide	0.92
	Benzene	1.03		Acetylene	Ethylene	0.94
Propane	n-Butane	1.01			Ethane	0.92
	Isobutane	1.01			Propylene	0.95
	n-Pentane	1.01			Propane	0.94
	Isopentane	1.02		Hydrogen chloride	Propane	0.88
	Benzene	1.00				

○ Paraffin–paraffin	◙ Nitrogen–paraffin
△ Olefin–olefin	▤ Nitrogen–olefin
▯ Paraffin–olefin	▲ Acetylene–paraffin
◊ Paraffin–aromatic	▼ Acetylene–olefin
◑ Olefin–aromatic	● Carbon dioxide–paraffin
◇ Paraffin–cycloparaffin	◕ Carbon dioxide–aromatic
▽ Olefin–cycloparaffin	◆ Carbon dioxide–olefin
◔ Argon–paraffin	▪ Hydrogen sulfide–paraffin
◒ Argon–olefin	▨ Hydrogen sulfide–carbon dioxide

Figure 4-1 Plot of pseudocritical temperature-interaction coefficients vs. ratios of molar critical volumes. *(From Ref. 2.)*

multicomponent mixture properties can then be estimated. In Table 4-1, k_{ij}^* values are tabulated for many binary pairs [2]. For simple binaries, k_{ij}^* can be approximately correlated with the ratio of the critical volumes of pure i and j, as shown in Fig. 4-1.

There is nothing rigorous in this approach. First, Eq. (4-3.5) may not be the best form for expressing T_{cij}. From molecular theory, the geometric mean of T_{ci} and T_{cj} could more easily be defended. Second, no ternary or higher interaction parameters are considered. Third, it is probably too much to expect that, for a given binary, there is but a single value of k_{ij}^* that is not a function of composition, temperature, or pressure. Only by experience have we obtained some confidence in approaches of this sort.

We consider next how the analytical equations of state mentioned in Chap. 3 can be modified for mixtures.

4-4   Second Virial Coefficients for Mixtures

The truncated virial equation shown in Sec. 3-5 is the only equation for real gases for which an exact relation is known for mixture coefficients:

$$B_m = \sum_i \sum_j y_i y_j B_{ij} \qquad (4\text{-}4.1)$$

For example, for a ternary mixture of 1, 2, and 3,

$$B_m = y_1^2 B_1 + y_2^2 B_2 + y_3^2 B_3 + 2y_1 y_2 B_{12} + 2y_1 y_3 B_{13} + 2y_2 y_3 B_{23} \qquad (4\text{-}4.2)$$

The pure component second virial coefficients B_1, B_2, and B_3 can often be found as described in Sec. 3-5 [e.g., Eqs. (3-5.4) to (3-5.6)] from the critical temperatures, critical pressures, and acentric factors of the pure materials. If one wishes to employ Eq. (3-5.4) to calculate the mixture interaction virials B_{ij}, combination rules must be devised to obtain T_{cij}, P_{cij}, and ω_{ij}. This problem has been discussed from a theoretical point of view by Leland and Chappelear [31] and Ramaiah and Stiel [45]. For typical engineering calculations involving normal fluids, the following simple rules are useful [43]:

$$T_{cij} = (T_{ci} T_{cj})^{1/2} (1 - k_{ij}) \qquad (4\text{-}4.3)$$

$$V_{cij} = \left[\frac{V_{ci}^{1/3} + V_{cj}^{1/3}}{2} \right]^3 \qquad (4\text{-}4.4)$$

$$Z_{cij} = \frac{Z_{ci} + Z_{cj}}{2} \qquad (4\text{-}4.5)$$

$$\omega_{ij} = \frac{\omega_i + \omega_j}{2} \qquad (4\text{-}4.6)$$

$$P_{cij} = \frac{Z_{cij} R T_{cij}}{V_{cij}} \qquad (4\text{-}4.7)$$

For molecules which do not differ greatly in size or chemical structure the binary constant k_{ij} can be set equal to zero. k_{ij} values for a variety of binary systems have been published [10]. Tsonopoulos [54] has provided additional k_{ij} values and has discussed their prediction and correlation. Tarakad and Danner [51] have also given guidelines for the estimation of k_{ij}. For binaries where both components fall into one of these categories (hydrocarbons, rare gases, permanent gases, carbon monoxide, perhalocarbons), k_{ij} may be estimated by

$$k_{ij} = 1 - \frac{8(V_{ci} V_{cj})^{1/2}}{(V_{ci}^{1/3} + V_{cj}^{1/3})^3} \qquad (4\text{-}4.8)$$

Also, if the molecule pairs contain a quantum gas (H_2, He, or Ne), modified critical constants are recommended [43]. Note that the T_{cij} in Eq. (4-4.3) is not the same quantity as the T_{cij} in Eq. (4-3.5).

A technique for estimating second virial coefficients of gas mixtures of simple fluids and heavy hydrocarbons has been given by Kaul and Prausnitz [26]. Maris and Stiel [35] have presented a method for estimating second virial coefficients of mixtures of polar compounds.

Example 4-1 Estimate the second virial coefficient for an equimolar methane (1)–n-butane (2) mixture at 444.3 K. $B_1 = -8.1$ cm^3/mol; $B_2 = -293.4$ cm^3/mol. Reference 62 gives $B_{12} = -63.4$ cm^3/mol, so for the mixture, $B_m = -107$ cm^3/mol.

solution

Component	T_c	V_c	Z_c	ω
1	190.6	99.2	0.288	0.012
2	425.2	255	0.274	0.199

Equation (4-4.8) gives $k_{12} = 0.036$ (Ref. 10 gives $k_{12} = 0.04$); Eqs. (4-4.3) through (4-4.7) give

$$T_{c12} = [(190.6)(425.2)]^{1/2}(1 - 0.036) = 274.4 \text{ K}$$

$$\omega_{12} = (0.5)(.012) + (0.5)(0.199) = 0.1055$$

$$Z_{c12} = (0.5)(0.288) + (0.5)(0.274) = 0.281$$

$$V_{c12} = \frac{(99.2^{1/3} + 255^{1/3})^3}{8} = 165.0 \text{ cm}^3/\text{mol}$$

$$P_{c12} = \frac{(0.281)(83.14)(273.3)}{165} = 38.7 \text{ bar}$$

$$T_{r12} = 444.3/274.4 = 1.619$$

Equations (3-5.5) and (3-5.6) give

$$B_{12}^{(0)} = -0.112 \qquad B_{12}^{(1)} = 0.116$$

Equation (3-5.4) gives

$$B_{12} = \frac{(83.14)(273.3)}{38.7}[-0.112 + (0.1055)(0.116)]$$

$$= -58.6 \text{ cm}^3/\text{mol}$$

Equation (4-4.1) gives

$$B_m = (0.5)^2(-8.1) + (2)(0.5)^2(-58.6) + (0.5)^2(-293.4)$$

$$= -105 \text{ cm}^3/\text{mol} \qquad (\text{error} = 2\%)$$

With $k_{12} = 0.036$, the predicted B_{12} is 4.8 cm^3/mol too high; with $k_{12} = 0$, the predicted B_{12} would be 6.3 cm^3/mol too low. Note that, in this example, the binary interaction parameter k_{12} was used in the estimation of the reduced temperature at which B_{12} was evaluated. This temperature was neither the pseudocritical nor the true critical temperature of the mixture, and it was not a function of the mixture composition. The pseudocritical approach offers an alternate solution method to Example 4-1. In theory, this approach is equivalent, but in practice it is less accurate.

Example 4-2 Repeat Example 4-1 by using the pseudocritical method.

solution From Table 4-1, $k_{12}^* = 1.11$. Equations (4-3.4) and (4-3.5) give

$$T_{c12} = \frac{(1.11)(190.6 + 425.2)}{2} = 341.8 \text{ K}$$

$$T_{cm} = (0.5)^2(190.6) + (2)(0.5)^2(341.8) + (0.5)^2(425.2)$$

$$= 324.8 \text{ K}$$

$$T_r = \frac{444.3}{324.8} = 1.3678$$

Equations (3-5.5) and (3-5.6) give $B^{(0)} = -0.1727$ and $B^{(1)} = 0.0928$; Eq. (4-3.2) gives

$$P_{cm} = \frac{(83.14)[(0.5)(0.288) + (0.5)(0.274)](324.8)}{(0.5)(99.2) + (0.5)(255)}$$

$$= 42.85 \text{ bar}$$

Equation (3-5.4) gives

$$B_m = \frac{(83.14)(324.8)}{42.85} [-0.1727 + (0.1055)(0.0928)]$$

$$= -103 \text{ cm}^3/\text{mol} \quad (error = 4\%)$$

If k_{12}^* were taken as zero, the answer would be $B_m = -89 \text{ cm}^3/\text{mol}$, for an error of 17%. This example illustrates how k_{12}^* is related to k_{12}.

4-5 Mixing Rules for Redlich-Kwong-Type Equations of State

The mixing rules recommended for all two-constant cubic equations of state (i.e., van der Waals, Redlich-Kwong, Soave, and Peng-Robinson) are

$$a_m = \sum_i \sum_j y_i y_j (a_i a_j)^{1/2} (1 - \bar{k}_{ij}) \tag{4-5.1}$$

$$b_m = \sum_i y_i b_i \tag{4-5.2}$$

a_i and b_i are given in Table 3-5. Some values of the binary interaction coefficient $\bar{k}_{ij}$ for the Soave and Peng-Robinson equations are given in Table 4-2. A more extensive tabulation is given in Ref. 28. Values for $\bar{k}_{ij}$ for specific systems and as a function of temperature are given in [9, 16, 23, 25, 33]. For hydrocarbon pairs, $\bar{k}_{ij}$ is usually taken as zero. If all $\bar{k}_{ij}$ are zero, Eq. (4-5.1) reduces to

$$a_m = \left(\sum_i y_i a_i^{1/2} \right)^2 \tag{4-5.3}$$

It can be shown that the second virial coefficient B is given by

$$B = b - \frac{a}{RT} \tag{4-5.4}$$

This provides a relation between $\bar{k}_{ij}$ and the k_{ij} in Eq. (4-4.3). In fact,

TABLE 4-2 $\overline{k}_{ij}$ **Values for Soave (SRK) and Peng-Robinson (PR) Equations [28]†**

	Carbon dioxide		Hydrogen sulfide		Nitrogen		Carbon monoxide	
	SRK	PR	SRK	PR	SRK	PR	SRK	PR
Methane	0.093	0.092			0.028	0.031	0.032	0.030
Ethylene	0.053	0.055	0.085	0.083	0.080	0.086		
Ethane	0.136	0.132			0.041	0.052	-0.028	-0.023
Propylene	0.094	0.093			0.090	0.090		
Propane	0.129	0.124	0.088	0.088	0.076	0.085	0.016	0.026
Isobutane	0.128	0.120	0.051	0.047	0.094	0.103		
n-Butane	0.143	0.133			0.070	0.080		
Isopentane	0.131	0.122			0.087	0.092		
n-Pentane	0.131	0.122	0.069	0.063	0.088	0.100		
n-Hexane	0.118	0.110			0.150	0.150		
n-Heptane	0.110	0.100			0.142	0.144		
n-Decane	0.130	0.114						
Carbon dioxide			0.099	0.097	-0.032	-0.017		
Cyclohexane	0.129	0.105						
Benzene	0.077	0.077			0.153	0.164		
Toluene	0.113	0.106						

†For a more complete list, see Ref. 28, pages 771–793.

setting $\overline{k}_{ij}$ equal to zero is equivalent to using Eq. (4-4.8) to calculate k_{ij} in a cross-virial-coefficient calculation [52]. Note that, once a and b for the mixture (a_m and b_m) are determined, computations proceed as though a and b were for a pure component (unless derivatives with respect to composition are required as with fugacity coefficients). In this approach, a pseudocritical temperature and pressure are not determined, although they could be. The pseudocritical temperature and pressure for the Soave equation are, for example, given by

$$T_{cm} = \frac{\sum_i \sum_j y_i y_j (a_i a_j)^{1/2}(1 - \overline{k}_{ij})}{\Omega_a R^2 \sum_i y_i T_{ci}/P_{ci}} \tag{4-5.5}$$

and

$$\frac{T_{cm}}{P_{cm}} = \sum_i \frac{y_i T_{ci}}{P_{ci}} \tag{4-5.6}$$

where

$$a_i = \frac{\Omega_a\{1 + fw_i[1 - (T_{cm}/T_{ci})^{1/2}]\}^2 R^2 T_{ci}^2}{P_{ci}} \tag{4-5.7}$$

fw_i is given in Table 3-5 and $\Omega_a = 0.42748$. Equation (4-5.5) must be solved iteratively, since a_i depends on T_{cm}.

Gray et al. [19] have reviewed some of the methods [14, 18, 20, 32, 38, 39, 63] for using the Soave equation for hydrogen-containing mixtures,

and Abbott [1] has presented mixing rules for cubic equations with more than the two parameters a and b.

Peneloux's correction to the mixture volumes is given by

$$c_m = \sum_i y_i c_i \tag{4-5.8}$$

The procedure for using this correction is the same as for pure components (which was dicussed in Sec. 3-6):

$$V = V_{SRK} - c_m \tag{4-5.9}$$

V_{SRK} is the volume predicted by the Soave equation; c_m is the correction for the mixture from Eq. (4-5.8); and V is the corrected volume.

4-6   Mixing Rules for the Lee-Kesler Equation

Numerous sets of mixing rules have been proposed for the Lee-Kesler method [2, 5, 29, 44, 47, 57, 60]. Those shown in Table 4-3 are recommended by Knapp et al. [28, 42]. These rules yield values of the mixture pseudocritical properties (T_{cm}, P_{cm}, V_{cm}, and ω_m) from which reduced mixture properties can be determined. Computations then proceed as for a pure component.

Sample values of the binary interaction coefficient k'_{ij} are given in Table 4-4. Values of k'_{ij} have been correlated with pure component properties as shown in Figs. 4-2 to 4-5 [42]. Values of k'_{ij} determined from experimental data, such as those in Table 4-4, are preferred to those estimated from Figs. 4-2 to 4-5, but estimates from the figures are better than taking k_{ij} to be unity. Figure 4-4 often provides reasonable estimates for hydrogen sulfide–hydrocarbon systems [42]. More detailed figures and additional values are given in Refs. 42 and 28. For hydrogen and helium, modified critical properties [43] should be used.

TABLE 4-3   Mixing Rules for the Lee-Kesler Equation [42]

$$T_{cm} = \frac{1}{V_{cm}^{1/4}} \sum_i \sum_j y_i y_j V_{cij}^{1/4} T_{cij} \tag{4-6.1}$$

$$V_{cm} = \sum_i \sum_j y_i y_j V_{cij} \tag{4-6.2}$$

$$\omega_m = \sum_i y_i \omega_i \tag{4-6.3}$$

$$T_{cij} = (T_{ci} T_{cj})^{1/2} k'_{ij} \tag{4-6.4}$$

$$V_{cij} = \tfrac{1}{8} (V_{ci}^{1/3} + V_{cj}^{1/3})^3 \tag{4-6.5}$$

$$P_{cm} = (0.2905 - 0.085 \omega_m) R T_{cm} / V_{cm} \tag{4-6.6}$$

TABLE 4-4   Binary Parameters k'_{ij} for the Lee-Kesler Method [42]

System	k'_{ij}	System	k'_{ij}
Methane-ethane	1.052	Ethylene-n-butane	0.998
-ethylene	1.014	-benzene	1.094
-propane	1.113	-n-heptane	1.163
-propylene	1.089	Acetylene-ethylene	0.948
-n-butane	1.171	Propane-propylene	0.992
-isobutane	1.155	-n-butane	1.003
-n-pentane	1.240	-isobutane	1.003
-isopentane	1.228	-n-pentane	1.006
-n-hexane	1.304	-isopentane	1.009
-cyclohexane	1.269	-n-hexane	1.047
-benzene	1.234	-cyclohexane	1.037
-n-heptane	1.367	-benzene	1.011
-n-octane	1.423	-n-heptane	1.067
-n-nonane	1.484	-n-octane	1.090
-n-decane	1.533	-n-nonane	1.115
Ethane-ethylene	0.991	-n-decane	1.139
-propane	1.010	Propylene-n-butane	1.010
-propylene	1.002	-isobutane	1.009
-n-butane	1.029	-isobutene	1.006
-isobutane	1.036	n-Butane-isobutane	1.001
-n-pentane	1.064	-n-pentane	0.994
-isopentane	1.070	-isopentane	0.998
-n-hexane	1.106	-n-hexane	1.018
-cyclohexane	1.081	-cyclohexane	1.008
-benzene	1.066	-benzene	0.999
-n-heptane	1.143	-n-heptane	1.027
-n-octane	1.165	-n-octane	1.046
-n-nonane	1.214	-n-nonane	1.064
-n-decane	1.237	-n-decane	1.078

4.7   Interaction Parameters—General Discussion

A frequently asked question is "Can values of k_{ij} from one equation of state be used in another equation of state?" To answer the question, one must first remember that all interaction parameters are empirical. If a k_{ij}
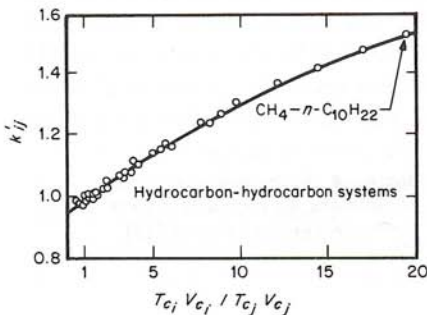
Figure 4-2 Correlation of binary parameters k'_{ij} for hydrocarbon-hydrocarbon systems, including aromatics [42].
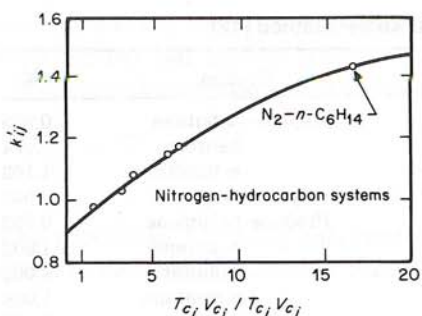
Figure 4-3 Correlation of binary parameters k'_{ij} for nitrogen-hydrocarbon systems [42].

for one equation is available, then mixture data are probably available. To use a different equation, these data should be regressed to find the best interaction parameter for the new equation. If data at different temperatures and pressures or data of a different type (*PVT* data instead of *VLE* data, for example) are used, a slightly different k_{ij} will likely be obtained. The important thing to remember is that k_{ij} values have no theoretical basis; they are empirical, and their role is to help overcome deficiencies in corresponding states theory, or deficiencies in a particular model's ability to describe what we perceive to be corresponding states behavior.

But even when one does not have access to a regression program, it is often possible to estimate an interaction parameter for one model from a value for another model. If all models were exact, they would predict identical pseudocritical temperatures and second virial coefficients. Thus, the T_{c_m}'s in Eqs. (4-3.4), (4-5.5), and (4-6.1) are all about the same number. The three equations contain, respectively, k^*_{ij}, $\bar{k}_{ij}$, and k'_{ij}. By equating T_{c_m} from Eqs. (4-3.4) and (4-5.5), one could, for example, estimate k^*_{ij} from $\bar{k}_{ij}$. The second virial coefficient expressions, Eqs. (4-4.1) and (4-5.4), provide a relation between k_{ij} and $\bar{k}_{ij}$. These interaction parameters are numerically different, but the mixture virial coefficients they predict should be about the same number [36]. k^*_{ij} and k_{ij} can be related by the technique illustrated by Examples 4-1 and 4-2.
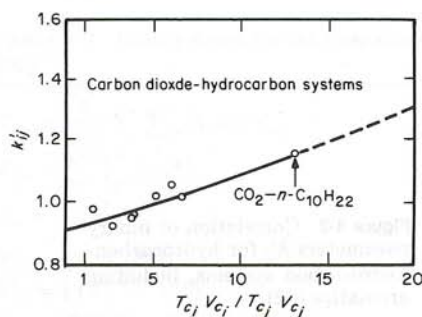
Figure 4-4 Correlation of binary parameters k'_{ij} for carbon dioxide–hydrocarbon systems [42].
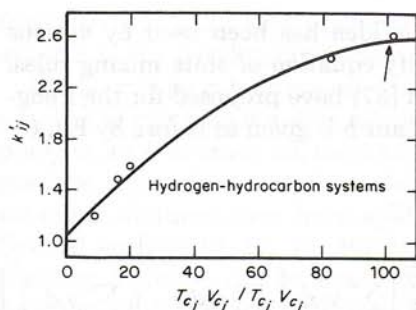
Figure 4-5 Correlation of binary parameters k'_{ij} for hydrogen-hydrocarbon systems. The arrow indicates data for the H_2–C_7H_{16} system [42].

4-8   Recent Developments in Mixing Rules

Numerous modifications to traditional mixing rules have been suggested. Some are the result of empirical studies [42]; others have resulted from a theoretical analysis [34]. Still others have been suggested to overcome shortcomings of the traditional mixing rules which arise in specific applications. Two such applications are for mixtures which contain polar molecules or which contain a large number of components.

For systems with even modest deviations from ideal solution behavior, a single binary parameter [for example, $\bar{k}_{ij}$ in Eq. (4-5.1)] often is a weak function of composition and temperature. Often this dependence is small and can be ignored, but for polar molecules, the variation in the interaction parameter with temperature and composition can become significant. Techniques for modifying equations of state to account for this behavior fall roughly into three categories. The categories include reaction models, local composition models, and empirical extensions. All the methods require more than one adjustable parameter per binary.

A method developed by Gmehling et al. [17] assumes that reactions occur among all the polar molecules in a mixture. The model also assumes pure polar compounds exist as an equilibrium mixture of monomers and dimers. Disadvantages of the model are (1) there are a large number of monomer-dimer species, (2) computations are complex because a combined reaction and phase equilibria problem must be solved iteratively, and (3) three or four parameters are required for each pure component. Advantages of the model are that only two adjustable parameters per binary are required and the model does work for mixtures of polar molecules. Only binary mixtures were examined in the original paper, but Buck [6] has extended the model to a seven-component system.

Local composition models, also called two-fluid theories, have as their underlying premise that the composition is not uniform throughout a binary mixture. For example, in a mixture of components A and B, if A molecules are more attracted to other A molecules than to B molecules, the "local mole fraction" of A around another A molecule will be greater

than the bulk mole fraction of A. This idea has been used by various authors [30, 49, 56, 58, 59, 61] to modify equation-of-state mixing rules. The mixing rule Mathias and Copeman [37] have proposed for the Peng-Robinson equation is typical. The constant b is given as before by Eq. (4-5.2), but

$$a_m = \sum_i \sum_j y_i y_j (a_i a_j)^{1/2} (1 - \overline{k}_{ij})$$
$$+ \frac{1}{2bRT\sqrt{2}} \ln \left[\frac{V + b + b\sqrt{2}}{V + b - b\sqrt{2}} \right] \sum_i y_i a_{ci}^2 \left[\sum_j y_j d_{ji}^2 - \left(\sum_j y_j d_{ji} \right)^2 \right]$$

$$(4\text{-}8.1)$$

where $a_{ci} = 0.45724 R^2 T_c^2 / P_c$ and a_i is given in Table 3-5: $\overline{k}_{ij}$ is symmetric, but d_{ij} is not. That is, $d_{ij} \neq d_{ji}$, but $\overline{k}_{ij} = \overline{k}_{ji}$. Also, $\overline{k}_{ii} = d_{ii} = 0$. Thus, in the above formulation, there are three parameters per binary, $\overline{k}_{12}$, d_{12}, and d_{21}. Local composition mixing rules as applied by other authors vary in the number of parameters used and in the equation of state to which the mixing rules are applied. Some forms do not reduce to a quadratic mixing rule at low densities as is required by the virial equation. Equation (4-8.1) does not have this shortcoming because, as V approaches infinity, the second term in Eq. (4-8.1) goes to zero. With this additional volume dependence, the equation is no longer cubic in volume.

All the local composition models require at least two parameters per binary. Several empirical forms which are simpler than Eq. (4-8.1) have been presented, but they still allow the inclusion of an additional binary parameter. Panagiotopoulos [41] suggests that Eq. (4-5.1) be replaced by

$$a_m = \sum_i \sum_j y_i y_j \left[(a_i a_j)^{1/2} (1 - \overline{k}_{ij}) + \frac{b_m}{VRT} (y_i \lambda_{ij} + y_j \lambda_{ji}) \right] \qquad (4\text{-}8.2)$$

where $\qquad \lambda_{ij} = -\lambda_{ji}$ $\qquad\qquad\qquad\qquad\qquad\qquad (4\text{-}8.3)$

In Eq. (4-8.1), there are three parameters per binary; in Eq. (4-8.2) there are two. Both of these equations make $\overline{k}_{ij}$, as defined in Eq. (4-5.1), a linear function of composition. The composition dependence expressed by Eq. (4-8.2) is obtained from Eq. (4-8.1) if d_{ij} is set equal to minus d_{ji}. Burcham et al. [7] have examined the case when one of the two d parameters in Eq. (4-8.1) is set equal to zero.

Several authors have added a second binary interaction parameter ϵ_{ij} in the b constant [8, 15, 49, 55], i.e.

$$b_m = \sum_i \sum_j y_i y_j \frac{(b_i + b_j)}{2} (1 - \epsilon_{ij}) \qquad\qquad\qquad (4\text{-}8.4)$$

(See also Sec. 8-12.) Efforts to apply equations of state to polar molecules are still in the development stage. It is not yet clear which form is best.

All the mixing rules presented thus far in this chapter are for a discrete number of components. For mixtures with a very large number of components, such as crude oil, the computations required to evaluate the summations many times can be prohibitively expensive. Traditionally these complex mixtures have been split into fractions of pseudocomponents. Several authors [3, 12, 13, 46] have developed the idea whereby these complex mixtures can be described by a single, continuous distribution function. Summations are replaced by integrals with a corresponding increase in computational efficiency. Cotterman et al. [12, 13] have used this idea along with a cubic equation of state and have presented the associated equations.

4-9   Densities of Liquid Mixtures

Mixing rules for both the modified Rackett and Hankinson equations have been published and are given below. The modified Rackett equation for mixtures at their bubble points is [50]

$$V_m = R \left(\sum_i \frac{x_i T_{ci}}{P_{ci}} \right) Z_{RA_m}^{[1 + (1 - T_r)^{2/7}]} \tag{4-9.1}$$

$$Z_{RA_m} = \sum_i x_i Z_{RA_i} \tag{4-9.2}$$

where $T_r = T/T_{cm}$ and the Chueh-Prausnitz rules [11, 54] are recommended [50] for T_{cm}:

$$T_{cm} = \sum_i \sum_j \phi_i \phi_j T_{cij} \tag{4-9.3}$$

$$\phi_i = \frac{x_i V_{ci}}{\sum_i x_i V_{ci}} \tag{4-9.4}$$

$$T_{cij} = (1 - k_{ij})(T_{ci} T_{cj})^{1/2} \tag{4-9.5}$$

$$1 - k_{ij} = \frac{8(V_{ci} V_{cj})^{1/2}}{(V_{ci}^{1/3} + V_{cj}^{1/3})^3} \tag{4-9.6}$$

Mixing rules recommended [22] for the Hankinson-Brobst-Thomson equation are

$$T_{cm} = \frac{\sum_i \sum_j x_i x_j V_{ij}^* T_{cij}}{V_m^*} \tag{4-9.7}$$

$$V_m^* = \tfrac{1}{4}\left[\sum_i x_i V_i^* + 3\left(\sum_i x_i V_i^{*2/3}\right)\left(\sum_i x_i V_i^{*1/3}\right)\right]$$ (4-9.8)

$$V_{ij}^* T_{cij} = (V_i^* T_{ci} V_j^* T_{cj})^{1/2}$$ (4-9.9)

$$\omega_{SRK_m} = \sum_i x_i \omega_{SRK_i}$$ (4-9.10)

$$P_{cm} = \frac{(0.291 - 0.080\omega_{SRK_m})RT_{cm}}{V_m^*}$$ (4-9.11)

In the HBT compressed liquid correlation Eq. (3-11.5), P_{vp_m} for a mixture is calculated by

$$P_{vp_m} = P_{cm} P_{rm}$$ (4-9.12)

P_{cm} is from Eq. (4-9.11), and P_{rm} is calculated from the generalized Riedel vapor pressure equation

$$\log_{10} P_{rm} = P_{rm}^{(0)} + \omega_{SRK_m} P_{rm}^{(1)}$$ (4-9.13)

$$P_{rm}^{(0)} = 5.8031817 \log_{10} T_{rm} + 0.07608141\alpha$$ (4-9.14)

$$P_{rm}^{(1)} = 4.86601(\log_{10} T_{rm} + 0.03721754\alpha)$$ (4-9.15)

$$\alpha = 35.0 - \frac{36.0}{T_{rm}} - 96.736 \log_{10} T_{rm} + T_{rm}^6$$ (4-9.16)

and

$$T_{rm} = \frac{T}{T_{cm}}$$ (4-9.17)

Teja [52] and Teja and Sandler [53] have calculated densities of LNG mixtures and CO_2–crude oil systems with Eq. (3-7.5) in which the two reference fluids were methane and either butane or decane. While they obtained very accurate results, their particular approach did require that binary interaction parameters be determined from binary density data.

Example 4-3   Calculate the volume of a saturated liquid mixture of 50.2 mole percent CO_2 (1) and 49.8 mole percent n-butane (2) at 344.26 K (160°F). Repeat for compressed liquid at 344.26 K and 345 bar (5000 psia). Experimental values [40] are V^L = 99.13 cm^3/mol at the bubble point pressure of 64.8 bar and V^L = 78.22 cm^3/mol at 345 bar.

solution   With T_c, ω_{SRK}, V^*, and Z_{RA} from Table 3-10 and V_c and P_c from Appendix A,

	T_c, K	P_c, bar	ω_{SRK}	V^*, cm^3/mol	Z_{RA}	V_c, cm^3/mol
CO_2	304.15	73.8	0.2373	93.8	0.2722	93.9
$n-C_4H_{10}$	425.18	38.0	0.2008	254.4	0.2730	255.0

HBT METHOD FOR SATURATED VOLUME   Equations (4-9.7) to (4-9.10) give

$\omega_{SRK_m} = 0.2191$ $V_m^* = 167.3 \text{ cm}^3/\text{mol}$ and $T_{cm} = 369.56 \text{ K}$

Thus $T_r = \dfrac{344.26}{369.56} = 0.9315$

From Eqs. (3-11.2) and (3-11.3),

$V_r^{(0)} = 0.5653$ and $V_r^{(\delta)} = 0.1698$.

Equation (3-11.1) then gives

$\quad V_s = (167.3)(0.5653)[1 - (0.219)(0.1698)]$

$\qquad = 91.0 \text{ cm}^3/\text{mol}$ (error = 8%)

MODIFIED RACKETT.   Equations (4-9.2) to (4-9.6) give

$\quad 1 - k_{12} = 0.959$ $T_{c12} = 345.0 \text{ K}$ $\phi_1 = 0.2704$

$\qquad \phi_2 = 0.7296$ $Z_{RA_m} = 0.2726$ and $T_{cm} = 384.7 \text{ K}$

Thus, $T_r = 0.895$, and Eq. (4-9.1) then gives

$\quad V = 87.5 \text{ cm}^3/\text{mol}$ (error = 12%)

HBT METHOD FOR COMPRESSED LIQUID.   Equation (4-9.11) gives

$$P_{cm} = \frac{[0.291 - (0.080)(0.2191)](83.14)(369.56)}{167.3}$$

$\qquad = 50.23 \text{ bar}$

Equations (3-11.6) to (3-11.8) give

$\quad c = 0.0861488 + (0.0344483)(0.2191) = 0.09370$

$\quad e = 135.0$

$\quad \dfrac{\beta}{P_c} = 0.2727$

$\quad \beta = 13.72$

Equations (4-9.12) to (4-9.17) give

$$\alpha = 35.0 - \frac{36.0}{0.9314} - 96.736 \log_{10} 0.9314 + (0.9314)^6$$

$\qquad = -0.01298$

$\quad P_{rm}^{(1)} = -0.1522$

$\quad P_{rm}^{(0)} = -0.1797$

$\quad \log_{10} P_{rm} = -0.1796 - (0.2191)(0.1522)$

$\qquad P_{rm} = 0.612$

$\qquad P_{vpm} = (0.612)(50.22)$

$\qquad = 30.75$

Equation (3-11.5) gives

$$V = (91.1)(1 - 0.0937 \ln\left(\frac{13.69 + 345}{13.69 + 30.75}\right)$$

$\qquad = 73.2 \text{ cm/mol}$ (error 6%)

The errors in this example are atypical. Tests with hydrocarbon mixtures and mixtures of hydrocarbons with other light gases gave much smaller errors for both the modified Rackett and HBT methods.

Recommendation

To estimate the volume of both saturated and compressed liquid mixtures, use the HBT correlations, Eqs. (3-11.1) and (3-11.5). Mixing rules are given in Eqs. (4-9.7) to (4-9.17).

Notation

a	attractive parameter in cubic equations of state, $\text{bar} \cdot \text{cm}^6/\text{mol}^2$
b	repulsive parameter in cubic equations of state, cm^3/mol
B	second virial coefficient, cm^3/mol
c	Peneloux's volume correction, Eq. (4-5.8), cm^3/mol
d	local composition binary parameter, Eq. (4-8.1)
$k_{ij}, k_{ij}^*, \overline{k}_{ij}, k_{ij}'$	binary interaction parameter
P	pressure; P_c, critical pressure; P_r, reduced pressure, P/P_c; P_{c_m}, pseudocritical mixture pressure, bar
Q	generalized property
R	gas constant, see Table 3-1
T	temperature; T_c, critical temperature; T_r, reduced temperature, T/T_c; T_{cT}, true critical temperature of a mixture; T_{c_m}, pseudocritical mixture temperature, K
V	volume; V_c, critical volume; V_r, reduced volume, V/V_c; V_{cT}, true critical volume for a mixture; V_{c_m}, pseudocritical mixture volume, cm^3/mol
V^*	parameter in HBT correlation
x	mole fraction in the liquid phase
y	mole fraction in the vapor phase, or in some cases in both the liquid and vapor phases
Z_c	critical compressibility factor
Z_{RA}	Rackett compressibility factor

GREEK

α	function of T_r; see Eq. (4-9.16)
ϕ	volume fraction, Eqs. (4-9.3) and (4-9.4)
ω_{SRK}	parameter in HBT correlation, Eq. (4-9.10)

SUPERSCRIPTS

L	liquid
V	vapor

SUBSCRIPTS

c	critical
j	component j
ij	interaction between i and j
m	mixture

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Thermodynamic Properties

5-1 Scope

In this chapter we first develop relations to calculate the Helmholtz and Gibbs energies, enthalpies, entropies, and fugacity coefficients. These relations are then used with equation-of-state correlations from Chap. 3 to develop estimation techniques for enthalpy and entropy departure functions and fugacity-pressure ratios for pure components and mixtures. In Sec. 5-5 methods are presented for determining the heat capacities of real gases. The true critical properties of mixtures are discussed in Sec. 5-6, and heat capacities of liquids are treated in Sec. 5-7. Fugacity coefficients of components in gas mixtures are considered in Sec. 5-8.

5-2 Fundamental Thermodynamic Principles

Enthalpy, internal energy, entropy, fugacity, etc., are useful thermodynamic properties. In analyzing or designing process equipment, a variation in these properties can often be related to operating variables, e.g., the temperature rise of a fluid in a heat exchanger. It is therefore important to estimate such property variations as the temperature, pressure, and other independent variables of a system change.

The variation of any thermodynamic property between two states is independent of the path chosen to pass from one state to the other. For example, with a pure fluid or a mixture of a fixed composition, if the dif-

ference in enthalpy between states P_1, T_1 and P_2, T_2 is desired, there are an infinite number of possible calculational paths, all of which give the same numerical result. Two of the most obvious are illustrated in Eqs. (5-2.2) and (5-2.3):

$$H = f(P, T)$$

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial H}{\partial T}\right)_P dT \tag{5-2.1}$$

$$H_2 - H_1 = \int_{P_1}^{P_2} \left(\frac{\partial H}{\partial P}\right)_{T_1} dP + \int_{T_1}^{T_2} \left(\frac{\partial H}{\partial T}\right)_{P_2} dT \tag{5-2.2}$$

$$H_2 - H_1 = \int_{P_1}^{P_2} \left(\frac{\partial H}{\partial P}\right)_{T_2} dP + \int_{T_1}^{T_2} \left(\frac{\partial H}{\partial T}\right)_{P_1} dT \tag{5-2.3}$$

In the first method, a stepwise process is visualized whereby the temperature is held constant at T_1 and the isothermal variation in H is determined from P_1 to P_2; this change is then added to the isobaric variation in H with T from T_1 to T_2 at pressure P_2. The second method is similar; but now the variation in H is first determined at P_1 from T_1 to T_2, and then the variation of H from P_1 to P_2 is determined at T_2. These paths are shown schematically in Fig. 5-1, where Eq. (5-2.2) is illustrated by path ADC, whereas Eq. (5-2.3) refers to path ABC. The net $\Delta H = H_2 - H_1$ represents the change AC. Obviously, any other convenient path is possible, for example, $AEFGHC$, but to calculate ΔH by this path, values of $(\partial H/\partial P)_T$ and $(\partial H/\partial T)_P$ must be available for the various isotherms and isobars.

The partial derivatives of enthalpy (or other thermodynamic properties) can be visualized as slopes of the isotherms or isobars in Fig. 5-1. To obtain numerical values of such derivatives, both a pressure and a tem-
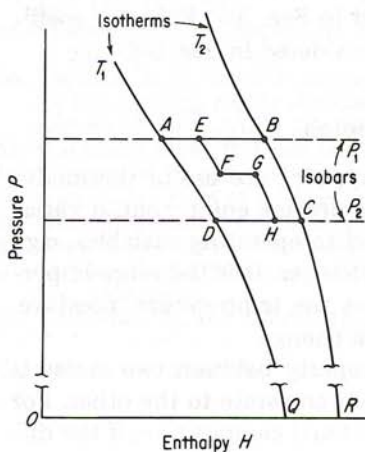
Figure 5-1 Schematic diagram showing possible isotherms and isobars for changes in enthalpy.

perature must be specified; i.e., values of these derivatives are also functions of two independent intensive variables in the same way that H, U, ... are functions of two such variables.

In Chap. 6, the quantity $(\partial H/\partial T)_{P^\circ}$ is considered. This derivative is called the *constant-pressure heat capacity* C_p°, and the superscript indicates that the pressure level is zero absolute pressure; i.e., the fluid is an ideal gas.

Rarely are heat capacities available at high pressures. Therefore, the usual path for determining $H_2 - H_1$ in Fig. 5-1 with values of C_p° is $AQRC$, that is,

$$\Delta H = \int_{P_1}^{P^\circ} \left(\frac{\partial H}{\partial P}\right)_{T_1} dP + \int_{T_1}^{T_2} C_p^\circ \, dT + \int_{P^\circ}^{P_2} \left(\frac{\partial H}{\partial P}\right)_{T_2} dP \qquad (5\text{-}2.4)$$

or $\quad \Delta H = (H^\circ - H_{P_1})_{T_1} + \int_{T_1}^{T_2} C_p^\circ \, dT - (H^\circ - H_{P_2})_{T_2} \qquad (5\text{-}2.5)$

The terms $(H^\circ - H_{P_1})_{T_1}$ and $(H^\circ - H_{P_2})_{T_2}$ are called *departure functions*. They relate a thermodynamic property (enthalpy in this case) at some P, T to a reference state ($P = 0$, for enthalpy) *at the same temperature*. It is shown in Sec. 5-3 that departure functions can be calculated solely from PVT data or, equivalently, from an equation of state. On the other hand, the term $\int C_p^\circ \, dT$ is evaluated in the ideal-gas state and values of C_p° are estimated as described in Chap. 6.

5-3 Departure Functions

Let $\mathcal{L}$ be the value of some thermodynamic property of a pure component (or a mixture with a fixed composition) at some P, T. If $\mathcal{L}^\circ$ is defined to be the value of $\mathcal{L}$ at the same temperature (and at the same composition if a mixture) but in an *ideal-gas state* and *at a reference pressure* P°, then a *departure function* is defined as $\mathcal{L} - \mathcal{L}^\circ$ or $\mathcal{L}^\circ - \mathcal{L}$. To complete the definition of the reference state, one must specify P° or V°; they are related by Eq. (5-3.1).

$$P^\circ V^\circ = RT \qquad (5\text{-}3.1)$$

There are four common choices for the reference state, i.e., P° = constant; V° = constant; $P^\circ = P$; or $V^\circ = V$. In the last two forms, the reference state values are not constants but vary with the system pressure or system specific volume.

As shown below, departure functions can be expressed in terms of the PVT properties of a fluid. Two general approaches are used. The first is more convenient if the PVT properties of a fluid are characterized by an equation of state explicit in pressure. All the analytical equations of state described in Chap. 3 are of this form. The second is more useful when temperature and pressure are the independent variables. The corresponding states correlations in Chap. 3, for example, are expressed as $Z = f(T_r, P_r)$.

For the first form, we develop the departure function for the Helmholtz energy A, and from this result all other departure functions can readily be obtained. At constant temperature and composition, the variation in the Helmholtz energy with molar volume V is

$$dA = -P \, dV \qquad (5\text{-}3.2)$$

Integrating at constant temperature and composition from the reference volume $V°$ to the system volume V gives

$$A - A° = - \int_{V°}^{V} P \, dV \qquad (5\text{-}3.3)$$

The evaluation of Eq. (5-3.3) is inconvenient, since one limit of the integration refers to the real state but the other to the reference, ideal-gas state. Thus, we break the integral into two parts:

$$A - A° = - \int_{\infty}^{V} P \, dV - \int_{V°}^{\infty} P \, dV \qquad (5\text{-}3.4)$$

The first integral requires real-gas properties, that is, $P = f(V)$ at constant temperature T, whereas the second is written for an ideal gas and can be integrated immediately. Before doing so, however, to avoid the difficulty introduced by the infinity limit, we add and subtract $\int_{\infty}^{V}(RT/V) \, dV$ from the right-hand side. Then

$$A - A° = - \int_{\infty}^{V} \left(P - \frac{RT}{V} \right) dV - RT \ln \frac{V}{V°} \qquad (5\text{-}3.5)$$

The departure function for A [Eq. (5-3.5)] depends upon the choice of $V°$. Note that $A - A°$ does *not* vanish even for an ideal gas unless $V°$ is chosen to equal V. Other departure functions are readily obtained from Eq. (5-3.5):

$$S - S° = \frac{-\partial}{\partial T} (A - A°)_V \qquad (5\text{-}3.6)$$

$$= \int_{\infty}^{V} \left[\left(\frac{\partial P}{\partial T} \right)_V - \frac{R}{V} \right] dV + R \ln \frac{V}{V°} \qquad (5\text{-}3.7)$$

$$H - H° = (A - A°) + T(S - S°) + RT(Z - 1) \qquad (5\text{-}3.8)$$

$$U - U° = (A - A°) + T(S - S°) \qquad (5\text{-}3.9)$$

$$G - G° = (A - A°) + RT(Z - 1) \qquad (5\text{-}3.10)$$

Also, although not strictly a departure function, the fugacity-pressure ratio can be expressed in a similar manner:

$$\ln \frac{f}{P} = \frac{A - A^\circ}{RT} + \ln \frac{V}{V^\circ} + (Z - 1) - \ln Z \tag{5-3.11}$$

$$= -\frac{1}{RT} \int_\infty^V \left(P - \frac{RT}{V} \right) dV + (Z - 1) - \ln Z$$

where $Z = PV/RT$.

Therefore, from any pressure-explicit equation of state and a definition of the reference state (P° or V°), all departure functions can readily be found.

Example 5-1 Derive the departure functions for a pure material or for a mixture of constant composition by using the Redlich-Kwong equation of state (3-6.1).

solution Using Eq. (3-6.1) and Table 3-5,

$$P = \frac{RT}{V - b} - \frac{a}{V(V + b)}$$

Then, with Eq. (5-3.5),

$$A - A^\circ = -\int_\infty^V \left[\frac{RT}{V - b} - \frac{RT}{V} - \frac{a}{V(V + b)} \right] dV - RT \ln \frac{V}{V^\circ}$$

$$= -RT \ln \frac{V - b}{V} - \frac{a}{b} \ln \frac{V + b}{V} - RT \ln \frac{V}{V^\circ}$$

For entropy, enthalpy, and internal energy with Eqs. (5-3.7) to (5-3.9),

$$S - S^\circ = -\left[\frac{\partial(A - A^\circ)}{\partial T} \right]_V$$

$$= R \ln \frac{V - b}{V} - \frac{a}{2bT} \ln \frac{V + b}{V} + R \ln \frac{V}{V^\circ}$$

$$H - H^\circ = (A - A^\circ) + T(S - S^\circ) + RT(Z - 1)$$

$$= PV - RT - \frac{3a}{2b} \ln \frac{V + b}{V}$$

$$= \frac{bRT}{V - b} - \frac{a}{(V + b)} - \frac{3a}{2b} \ln \frac{V + b}{V}$$

$$U - U^\circ = (A - A^\circ) + T(S - S^\circ) = -\frac{3a}{2b} \ln \frac{V + b}{V}$$

For $\ln(f/P)$, with Eq. (5-3.11), where

$$Z = \frac{PV}{RT} = \frac{V}{V - b} - \frac{a}{RT(V + b)}$$

we have

$$\ln \frac{f}{P} = \frac{b}{V - b} - \frac{a}{RT(V + b)} - \ln \frac{V - b}{V} - \frac{a}{bRT} \ln \frac{V + b}{V}$$

$$- \ln \left[\frac{V}{V - b} - \frac{a}{RT(V + b)} \right]$$

Finally, from Eq. (5-3.10)

$$G - G^\circ = \frac{bRT}{V - b} - \frac{a}{(V + b)} - RT \ln \frac{V - b}{V} - \frac{a}{b} \ln \frac{V + b}{V} - RT \ln \frac{V}{V^\circ}$$

From Eqs. (5-3.5) to (5-3.11), or with Example 5-1, one can see that the departure functions $H - H^\circ$, $U - U^\circ$, and $\ln(f/P)$ do not depend upon the value of the reference state pressure P° (or V°). In contrast, $A - A^\circ$, $S - S^\circ$, and $G - G^\circ$ do depend upon P° (or V°). Either of two common reference states is normally chosen. In the first, P° is set equal to a unit pressure, for example, 1 bar if that is the pressure unit chosen. Then, from Eq. (5-3.1), $V^\circ = RT$, but it is necessary to express R in the same units of pressure. In the second reference state, $P^\circ = P$, the system pressure. Then $V/V^\circ = Z$, the compressibility factor. Other reference states can be defined, for example, $V^\circ = V$, but the two noted above are the more common.

An alternate calculational path to obtain departure functions is more convenient if the equation of state is explicit in volume or if pressure and temperature are the independent variables. In such cases, we again choose as a reference state an ideal gas at the same temperature and composition as that of the system under study. The reference pressure is P°, and Eq. (5-3.1) applies. We begin, however, with the Gibbs energy rather than the Helmholtz energy. The analog to Eq. (5-3.4) is

$$G - G^\circ = \int_{P^\circ}^{P} V \, dP = \int_{0}^{P} V \, dP + \int_{P^\circ}^{0} V \, dP$$

$$= \int_{0}^{P} \left(V - \frac{RT}{P} \right) dP + RT \ln \frac{P}{P^\circ} \tag{5-3.12}$$

$$= RT \int_{0}^{P} (Z - 1) \, d \ln P + RT \ln \frac{P}{P^\circ} \tag{5-3.13}$$

For entropy,

$$S - S^\circ = \frac{-\partial}{\partial T} (G - G^\circ)_P$$

$$= R \int_{0}^{P} \left[1 - Z - T \left(\frac{\partial Z}{\partial T} \right)_P \right] d \ln P - R \ln \frac{P}{P^\circ} \tag{5-3.14}$$

and for the enthalpy and internal-energy departure functions,

$$H - H^\circ = (G - G^\circ) + T(S - S^\circ) \tag{5-3.15}$$

$$U - U^\circ = (G - G^\circ) + T(S - S^\circ) - RT(Z - 1) \tag{5-3.16}$$

The Helmholtz-energy departure function is

$$A - A^\circ = (G - G^\circ) - RT(Z - 1) \tag{5-3.17}$$

and

$$\ln \frac{f}{P} = \left(\frac{G - G^\circ}{RT} \right) - \ln \frac{P}{P^\circ} \tag{5-3.18}$$

Again, simple algebraic substitution shows that the departure functions $H - H°$, $U - U°$, and $\ln(f/P)$ do not depend upon the choice of $P°$ (or $V°$).

5-4 Evaluation of Departure Functions

The departure functions shown in Eqs. (5-3.5) to (5-3.11) or in Eqs. (5-3.12) to (5-3.18) can be evaluated with PVT data and, when necessary, a definition of the reference state. Generally, either an analytical equation of state or some form of the law of corresponding states is used to characterize PVT behavior, although, if available, experimental PVT data for a pure substance or a given mixture can be employed.

Departure functions from equations of state

Several analytical equations of state were introduced in Chap. 3. All are pressure-explicit. In the same manner as that shown in Example 5-1, departure functions can be determined. $A - A°$ and $S - S°$ for three equations of state are shown in Table 5-1. With $A - A°$ and $S - S°$, $H - H°$, $U - U°$, etc., are readily found from Eqs. (5-3.8) to (5-3.11). In each case reference is made to the appropriate equations or tables in Chaps. 3 and 4, where the characteristic parameters of the equation are defined.

The Lee-Kesler correlation [Eqs. (3-7.1) to (3-7.4)] is not shown in Table 5-1. To employ it to calculate thermodynamic properties, care must be exercised in following the procedure recommended by the authors. The method is illustrated with the enthalpy departure function, and analogous rules apply to the entropy departure function and fugacity-pressure ratio.

Given a pressure and temperature, the first step involves the calculation of the reduced temperature and pressure. If the fluid is pure, T_c and P_c values can be found in Appendix A or estimated by relations given in Chap. 2. For mixtures, the appropriate pseudocritical properties are determined from Eqs. (4-6.1) to (4-6.6). With T_r and P_r following the procedure given in Sec. 3-7, $V_r^{(0)}$, $V_r^{(R)}$, $Z^{(0)}$, and $Z^{(R)}$ are determined. From T_r, $V_r^{(0)}$, and $Z^{(0)}$ the simple fluid enthalpy departure function can then be found:

$$\left(\frac{H° - H}{RT_c}\right)^{(0)} = -T_r\left[Z^{(0)} - 1 - \frac{b_2 + 2b_3/T_r + 3b_4/T_r^2}{T_r(V_r^{(0)})}\right.$$
$$\left. - \frac{c_2 - 3c_3/T_r^2}{2T_r(V_r^{(0)})^2} + \frac{d_2}{5T_r(V_r^{(0)})^5} + 3E\right] \qquad (5\text{-}4.1)$$

where
$$E = \frac{c_4}{2T_r^3\gamma}\left\{\beta + 1 - \left[\beta + 1 + \frac{\gamma}{(V_r^{(0)})^2}\right]\exp\left[-\frac{\gamma}{(V_r^{(0)})^2}\right]\right\}$$
$$(5\text{-}4.2)$$

TABLE 5-1   Departure Functions for the Virial and Cubic Equations of State
Only $A - A°$ and $S - S°$ departure functions are given; $H - H°$, $U - U°$, $G - G°$, and $\ln (f/P)$ are readily obtained from Eqs. (5-3.8) to (5-3.11).

Virial, Secs. 3-5 and 4-4

$$Z = 1 + \frac{BP}{RT}$$

$$A - A° = RT \ln \frac{V}{V - B} - RT \ln \frac{V}{V°}$$

$$S - S° = -\frac{RT}{V - B}\frac{dB}{dT} - R \ln \frac{V}{V - B} + R \ln \frac{V}{V°}$$

B is given in Eqs. (3-5.3) and (4-4.1)

Cubic, Secs. 3-6 and 4-5

$$P = \frac{RT}{V - b} - \frac{a}{V^2 + uVb + wb^2}$$

$$A - A° = \frac{a}{b\sqrt{u^2 - 4w}} \ln \frac{2Z + B^*(u - \sqrt{u^2 - 4w})}{2Z + B^*(u + \sqrt{u^2 - 4w})} - RT \ln \frac{Z - B^*}{Z} - RT \ln \frac{V}{V°}$$

$$S - S° = R \ln \frac{Z - B^*}{Z} + R \ln \frac{V}{V°} - \frac{1}{b\sqrt{u^2 - 4w}}\frac{\partial a}{\partial T} \ln \frac{2Z + B^*(u - \sqrt{u^2 - 4w})}{2Z + B^*(u + \sqrt{u^2 - 4w})}$$

where
$$\frac{\partial a}{\partial T} = -\frac{R}{2}\left(\frac{\Omega_a}{T}\right)^{1/2} \sum_i \sum_j y_i y_j (1 - \overline{k}_{ij}) \left[f\omega_j \left(\frac{a_i T_{cj}}{P_{cj}}\right)^{1/2} + f\omega_i \left(\frac{a_j T_{ci}}{P_{ci}}\right)^{1/2} \right]$$

For the Soave Equation

$f\omega_i = 0.480 + 1.574\omega_i - 0.176\omega_i^2$
$\Omega_a = 0.42748$

For the Peng-Robinson Equation

$f\omega_i = 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2$
$\Omega_a = 0.45724$

Note: u, w, a_i, a, and b are given in Table 3-5 and Eqs. (4-5.1) and (4-5.2).

Next, using the same T_r but $V_r^{(R)}$ and $Z^{(R)}$, recompute Eq. (5-4.1) using the reference fluid constants in Table 3-7; call this departure function $[(H° - H)/RT_c]^{(R)}$. The departure function for the real fluid is then

$$\frac{H° - H}{RT_c} = \left(\frac{H° - H}{RT_c}\right)^{(0)} + \frac{\omega}{\omega^R}\left[\left(\frac{H° - H}{RT_c}\right)^{(R)} - \left(\frac{H° - H}{RT_c}\right)^{(0)}\right] \tag{5-4.3}$$

Equation (5-4.3) may be rewritten as

$$\frac{H° - H}{RT_c} = \left(\frac{H° - H}{RT_c}\right)^{(0)} + \omega\left(\frac{H° - H}{RT_c}\right)^{(1)} \tag{5-4.4}$$

if the deviation function for enthalpy is defined as

$$\left(\frac{H^\circ - H}{RT_c}\right)^{(1)} = \frac{1}{\omega^R}\left[\left(\frac{H^\circ - H}{RT_c}\right)^{(R)} - \left(\frac{H^\circ - H}{RT_c}\right)^{(0)}\right] \tag{5-4.5}$$

With Eqs. (5-4.1) and (5-4.5), Tables 5-2 and 5-3 were developed [47]. In these calculations ω^R was set equal to 0.3978. Tables 5-2 and 5-3 are presented graphically in [84].

Entropy

Analogous expressions for the entropy departure functions are

$$\left(\frac{S^\circ - S}{R}\right)^{(0)} = -\ln\frac{P^\circ}{P} - \ln Z^{(0)} + \frac{b_1 + b_3/T_r^2 + 2b_4/T_r^3}{V_r^{(0)}}$$
$$+ \frac{c_1 - 2c_3/T_r^3}{2(V_r^{(0)})^2} + \frac{d_1}{5(V_r^{(0)})^5} - 2E \tag{5-4.6}$$

$$\frac{S^\circ - S}{R} = \left(\frac{S^\circ - S}{R}\right)^{(0)} + \frac{\omega}{\omega^R}\left[\left(\frac{S^\circ - S}{R}\right)^{(R)} - \left(\frac{S^\circ - S}{R}\right)^{(0)}\right] \tag{5-4.7}$$

If Eq. (5-4.6) is written as

$$\frac{S^\circ - S}{R} = -\ln\frac{P^\circ}{P} + \left(\frac{S^\circ - S}{R}\right)^{(0)} + \omega\left(\frac{S^\circ - S}{R}\right)^{(1)} \tag{5-4.8}$$

the simple fluid entropy departure $(\ )^{(0)}$ and the deviation function $(\ )^{(1)}$ can be found in Tables 5-4 and 5-5.

Fugacity-pressure ratio

As with the enthalpy departure calculation,

$$\left(\ln\frac{f}{P}\right)^{(0)} = Z^{(0)} - 1 - \ln Z^{(0)} + \frac{B}{V_r^{(0)}} + \frac{C}{2(V_r^{(0)})^2} + \frac{D}{5(V_r^{(0)})^5} + E \tag{5-4.9}$$

$$\ln\frac{f}{P} = \left(\ln\frac{f}{P}\right)^{(0)} + \frac{\omega}{\omega^R}\left[\left(\ln\frac{f}{P}\right)^{(R)} - \left(\ln\frac{f}{P}\right)^{(0)}\right] \tag{5-4.10}$$

and when Eq. (5-4.10) is written as

$$\ln\frac{f}{P} = \left(\ln\frac{f}{P}\right)^{(0)} + \omega\left(\ln\frac{f}{P}\right)^{(1)} \tag{5-4.11}$$

the simple fluid and deviation functions can be found from Tables 5-6 and 5-7. (Note that $\log\frac{f}{P}$, not $\ln\frac{f}{P}$, is obtained from these tables.)

TABLE 5-2 Lee-Kesler Residual Enthalpy [47]

Simple fluid $\left(\dfrac{H^\circ - H}{RT_c}\right)^{(0)}$

T_r	P_r						
	0.010	0.050	0.100	0.200	0.400	0.600	0.800
0.30	6.045	6.043	6.040	6.034	6.022	6.011	5.999
0.35	5.906	5.904	5.901	5.895	5.882	5.870	5.858
0.40	5.763	5.761	5.757	5.751	5.738	5.726	5.713
0.45	5.615	5.612	5.609	5.603	5.590	5.577	5.564
0.50	5.465	5.463	5.459	5.453	5.440	5.427	5.414
0.55	0.032	5.312	5.309	5.303	5.290	5.278	5.265
0.60	0.027	5.162	5.159	5.153	5.141	5.129	5.116
0.65	0.023	0.118	5.008	5.002	4.991	4.980	4.968
0.70	0.020	0.101	0.213	4.848	4.838	4.828	4.818
0.75	0.017	0.088	0.183	4.687	4.679	4.672	4.664
0.80	0.015	0.078	0.160	0.345	4.507	4.504	4.499
0.85	0.014	0.069	0.141	0.300	4.309	4.313	4.316
0.90	0.012	0.062	0.126	0.264	0.596	4.074	4.094
0.93	0.011	0.058	0.118	0.246	0.545	0.960	3.920
0.95	0.011	0.056	0.113	0.235	0.516	0.885	3.763
0.97	0.011	0.054	0.109	0.225	0.490	0.824	1.356
0.98	0.010	0.053	0.107	0.221	0.478	0.797	1.273
0.99	0.010	0.052	0.105	0.216	0.466	0.773	1.206
1.00	0.010	0.051	0.103	0.212	0.455	0.750	1.151
1.01	0.010	0.050	0.101	0.208	0.445	0.728	1.102
1.02	0.010	0.049	0.099	0.203	0.434	0.708	1.060
1.05	0.009	0.046	0.094	0.192	0.407	0.654	0.955
1.10	0.008	0.042	0.086	0.175	0.367	0.581	0.827
1.15	0.008	0.039	0.079	0.160	0.334	0.523	0.732
1.20	0.007	0.036	0.073	0.148	0.305	0.474	0.657
1.30	0.006	0.031	0.063	0.127	0.259	0.399	0.545
1.40	0.005	0.027	0.055	0.110	0.224	0.341	0.463
1.50	0.005	0.024	0.048	0.097	0.196	0.297	0.400
1.60	0.004	0.021	0.043	0.086	0.173	0.261	0.350
1.70	0.004	0.019	0.038	0.076	0.153	0.231	0.309
1.80	0.003	0.017	0.034	0.068	0.137	0.206	0.275
1.90	0.003	0.015	0.031	0.062	0.123	0.185	0.246
2.00	0.003	0.014	0.028	0.056	0.111	0.167	0.222
2.20	0.002	0.012	0.023	0.046	0.092	0.137	0.182
2.40	0.002	0.010	0.019	0.038	0.076	0.114	0.150
2.60	0.002	0.008	0.016	0.032	0.064	0.095	0.125
2.80	0.001	0.007	0.014	0.027	0.054	0.080	0.105
3.00	0.001	0.006	0.011	0.023	0.045	0.067	0.088
3.50	0.001	0.004	0.007	0.015	0.029	0.043	0.056
4.00	0.000	0.002	0.005	0.009	0.017	0.026	0.033

				P_r				
1.000	1.200	1.500	2.000	3.000	5.000	7.000	10.000
5.987	5.975	5.957	5.927	5.868	5.748	5.628	5.446
5.845	5.833	5.814	5.783	5.721	5.595	5.469	5.278
5.700	5.687	5.668	5.636	5.572	5.442	5.311	5.113
5.551	5.538	5.519	5.486	5.421	5.288	5.154	4.950
5.401	5.388	5.369	5.336	5.270	5.135	4.999	4.791
5.252	5.239	5.220	5.187	5.121	4.986	4.849	4.638
5.104	5.091	5.073	5.041	4.976	4.842	4.704	4.492
4.956	4.945	4.927	4.896	4.833	4.702	4.565	4.353
4.808	4.797	4.781	4.752	4.693	4.566	4.432	4.221
4.655	4.646	4.632	4.607	4.554	4.434	4.303	4.095
4.494	4.488	4.478	4.459	4.413	4.303	4.178	3.974
4.316	4.316	4.312	4.302	4.269	4.173	4.056	3.857
4.108	4.118	4.127	4.132	4.119	4.043	3.935	3.744
3.953	3.976	4.000	4.020	4.024	3.963	3.863	3.678
3.825	3.865	3.904	3.940	3.958	3.910	3.815	3.634
3.658	3.732	3.796	3.853	3.890	3.856	3.767	3.591
3.544	3.652	3.736	3.806	3.854	3.829	3.743	3.569
3.376	3.558	3.670	3.758	3.818	3.801	3.719	3.548
2.584	3.441	3.598	3.706	3.782	3.774	3.695	3.526
1.796	3.283	3.516	3.652	3.744	3.746	3.671	3.505
1.627	3.039	3.422	3.595	3.705	3.718	3.647	3.484
1.359	2.034	3.030	3.398	3.583	3.632	3.575	3.420
1.120	1.487	2.203	2.965	3.353	3.484	3.453	3.315
0.968	1.239	1.719	2.479	3.091	3.329	3.329	3.211
0.857	1.076	1.443	2.079	2.807	3.166	3.202	3.107
0.698	0.860	1.116	1.560	2.274	2.825	2.942	2.899
0.588	0.716	0.915	1.253	1.857	2.486	2.679	2.692
0.505	0.611	0.774	1.046	1.549	2.175	2.421	2.486
0.440	0.531	0.667	0.894	1.318	1.904	2.177	2.285
0.387	0.466	0.583	0.777	1.139	1.672	1.953	2.091
0.344	0.413	0.515	0.683	0.996	1.476	1.751	1.908
0.307	0.368	0.458	0.606	0.880	1.309	1.571	1.736
0.276	0.330	0.411	0.541	0.782	1.167	1.411	1.577
0.226	0.269	0.334	0.437	0.629	0.937	1.143	1.295
0.187	0.222	0.275	0.359	0.513	0.761	0.929	1.058
0.155	0.185	0.228	0.297	0.422	0.621	0.756	0.858
0.130	0.154	0.190	0.246	0.348	0.508	0.614	0.689
0.109	0.129	0.159	0.205	0.288	0.415	0.495	0.545
0.069	0.081	0.099	0.127	0.174	0.239	0.270	0.264
0.041	0.048	0.058	0.072	0.095	0.116	0.110	0.061

TABLE 5-3 Lee-Kesler Residual Enthalpy [47]

Deviation function $\left(\dfrac{H° - H}{RT_c}\right)^{(1)}$

T_r	P_r						
	0.010	0.050	0.100	0.200	0.400	0.600	0.800
0.30	11.098	11.096	11.095	11.091	11.083	11.076	11.069
0.35	10.656	10.655	10.654	10.653	10.650	10.646	10.643
0.40	10.121	10.121	10.121	10.120	10.121	10.121	10.121
0.45	9.515	9.515	9.516	9.517	9.519	9.521	9.523
0.50	8.868	8.869	8.870	8.872	8.876	8.880	8.884
0.55	0.080	8.211	8.212	8.215	8.221	8.226	8.232
0.60	0.059	7.568	7.570	7.573	7.579	7.585	7.591
0.65	0.045	0.247	6.949	6.952	6.959	6.966	6.973
0.70	0.034	0.185	0.415	6.360	6.367	6.373	6.381
0.75	0.027	0.142	0.306	5.796	5.802	5.809	5.816
0.80	0.021	0.110	0.234	0.542	5.266	5.271	5.278
0.85	0.017	0.087	0.182	0.401	4.753	4.754	4.758
0.90	0.014	0.070	0.144	0.308	0.751	4.254	4.248
0.93	0.012	0.061	0.126	0.265	0.612	1.236	3.942
0.95	0.011	0.056	0.115	0.241	0.542	0.994	3.737
0.97	0.010	0.052	0.105	0.219	0.483	0.837	1.616
0.98	0.010	0.050	0.101	0.209	0.457	0.776	1.324
0.99	0.009	0.048	0.097	0.200	0.433	0.722	1.154
1.00	0.009	0.046	0.093	0.191	0.410	0.675	1.034
1.01	0.009	0.044	0.089	0.183	0.389	0.632	0.940
1.02	0.008	0.042	0.085	0.175	0.370	0.594	0.863
1.05	0.007	0.037	0.075	0.153	0.318	0.498	0.691
1.10	0.006	0.030	0.061	0.123	0.251	0.381	0.507
1.15	0.005	0.025	0.050	0.099	0.199	0.296	0.385
1.20	0.004	0.020	0.040	0.080	0.158	0.232	0.297
1.30	0.003	0.013	0.026	0.052	0.100	0.142	0.177
1.40	0.002	0.008	0.016	0.032	0.060	0.083	0.100
1.50	0.001	0.005	0.009	0.018	0.032	0.042	0.048
1.60	0.000	0.002	0.004	0.007	0.012	0.013	0.011
1.70	0.000	0.000	0.000	-0.000	-0.003	-0.009	-0.017
1.80	-0.000	-0.001	-0.003	-0.006	-0.015	-0.025	-0.037
1.90	-0.001	-0.003	-0.005	-0.011	-0.023	-0.037	-0.053
2.00	-0.001	-0.003	-0.007	-0.015	-0.030	-0.047	-0.065
2.20	-0.001	-0.005	-0.010	-0.020	-0.040	-0.062	-0.083
2.40	-0.001	-0.006	-0.012	-0.023	-0.047	-0.071	-0.095
2.60	-0.001	-0.006	-0.013	-0.026	-0.052	-0.078	-0.104
2.80	-0.001	-0.007	-0.014	-0.028	-0.055	-0.082	-0.110
3.00	-0.001	-0.007	-0.014	-0.029	-0.058	-0.086	-0.114
3.50	-0.002	-0.008	-0.016	-0.031	-0.062	-0.092	-0.122
4.00	-0.002	-0.008	-0.016	-0.032	-0.064	-0.096	-0.127

			P_r				
1.000	1.200	1.500	2.000	3.000	5.000	7.000	10.000
11.062	11.055	11.044	11.027	10.992	10.935	10.872	10.781
10.640	10.637	10.632	10.624	10.609	10.581	10.554	10.529
10.121	10.121	10.121	10.122	10.123	10.128	10.135	10.150
9.525	9.527	9.531	9.537	9.549	9.576	9.611	9.663
8.888	8.892	8.899	8.909	8.932	8.978	9.030	9.111
8.238	8.243	8.252	8.267	8.298	8.360	8.425	8.531
7.596	7.603	7.614	7.632	7.669	7.745	7.824	7.950
6.980	6.987	6.997	7.017	7.059	7.147	7.239	7.381
6.388	6.395	6.407	6.429	6.475	6.574	6.677	6.837
5.824	5.832	5.845	5.868	5.918	6.027	6.142	6.318
5.285	5.293	5.306	5.330	5.385	5.506	5.632	5.824
4.763	4.771	4.784	4.810	4.872	5.008	5.149	5.358
4.249	4.255	4.268	4.298	4.371	4.530	4.688	4.916
3.934	3.937	3.951	3.987	4.073	4.251	4.422	4.662
3.712	3.713	3.730	3.773	3.873	4.068	4.248	4.497
3.470	3.467	3.492	3.551	3.670	3.885	4.077	4.336
3.332	3.327	3.363	3.434	3.568	3.795	3.992	4.257
3.164	3.164	3.223	3.313	3.464	3.705	3.909	4.178
2.471	2.952	3.065	3.186	3.358	3.615	3.825	4.100
1.375	2.595	2.880	3.051	3.251	3.525	3.742	4.023
1.180	1.723	2.650	2.906	3.142	3.435	3.661	3.947
0.877	0.878	1.496	2.381	2.800	3.167	3.418	3.722
0.617	0.673	0.617	1.261	2.167	2.720	3.023	3.362
0.459	0.503	0.487	0.604	1.497	2.275	2.641	3.019
0.349	0.381	0.381	0.361	0.934	1.840	2.273	2.692
0.203	0.218	0.218	0.178	0.300	1.066	1.592	2.086
0.111	0.115	0.108	0.070	0.044	0.504	1.012	1.547
0.049	0.046	0.032	-0.008	-0.078	0.142	0.556	1.080
0.005	-0.004	-0.023	-0.065	-0.151	-0.082	0.217	0.689
-0.027	-0.040	-0.063	-0.109	-0.202	-0.223	-0.028	0.369
-0.051	-0.067	-0.094	-0.143	-0.241	-0.317	-0.203	0.112
-0.070	-0.088	-0.117	-0.169	-0.271	-0.381	-0.330	-0.092
-0.085	-0.105	-0.136	-0.190	-0.295	-0.428	-0.424	-0.255
-0.106	-0.128	-0.163	-0.221	-0.331	-0.493	-0.551	-0.489
-0.120	-0.144	-0.181	-0.242	-0.356	-0.535	-0.631	-0.645
-0.130	-0.156	-0.194	-0.257	-0.376	-0.567	-0.687	-0.754
-0.137	-0.164	-0.204	-0.269	-0.391	-0.591	-0.729	-0.836
-0.142	-0.170	-0.211	-0.278	-0.403	-0.611	-0.763	-0.899
-0.152	-0.181	-0.224	-0.294	-0.425	-0.650	-0.827	-1.015
-0.158	-0.188	-0.233	-0.306	-0.442	-0.680	-0.874	-1.097

Discussion

In testing the departure functions presented in this chapter, only estimated values of $H° - H$ can be compared with experimental data; and even here, most reliable data are limited to simple hydrocarbons and the permanent light gases. Also, it is convenient to summarize at this point the methods for estimating molar volumes of gas mixtures.

Recommended methods for estimating the molar volumes of pure gases are given in Sec. 3-8 and those for pure liquids in Sec. 3-11. Liquid mixtures are treated in Sec. 4-9. The Lee-Kesler equation also has been used to calculate molar volumes of pure liquids and liquid mixtures of light hydrocarbons, but the methods described in Sec. 4-9 are generally more accurate.

Molar volumes for gas mixtures

No comprehensive test has been made of all estimation techniques. Authors of individual methods have made limited comparisons, as have the authors of this book. Generally, errors were found to be less than 2 to 3 percent, except near the critical point or for mixtures containing highly polar components in significant concentrations.

Recommendations to estimate the molar volume of hydrocarbon gas mixtures (including those with components associated with natural gas, for example, CO_2 and H_2S), are essentially the same as for pure gases. For small deviations from ideal-gas behavior, the truncated virial equation is satisfactory. Otherwise, use any of the other equations of state in Chaps. 3 and 4. Values of binary interaction coefficients (k_{ij}'s) determined from VLE data can be used in volume calculations; mixture volumes are much less sensitive to k_{ij} values than are VLE calculations.

To estimate the molar volumes of gas mixtures containing nonhydrocarbons, the Lee-Kesler equation may be used, even though it has not been critically evaluated for nonhydrocarbons; in most cases, binary interaction parameters are required for high accuracy. Equations such as those proposed by Gmehling et al. [26] and Vimalchand et al. [85, 86] are more complicated but have demonstrated some ability to describe the behavior of polar molecules.

The equations of state noted above for hydrocarbon and nonhydrocarbon mixtures are complex and normally require a computer for efficient utilization. Cubic equations of state may be slightly less accurate, but they are simpler in form. The truncated virial equation is the easiest of all equations of state to use, although for mixtures its accuracy may be poor unless care is taken to estimate the cross-coefficient B_{12}. Also, it should not be used if $\rho/\rho_c > 0.5$.

Enthalpy departures for pure gases and mixtures—recommendations

For hydrocarbons and hydrocarbon gas mixtures (including light gases such as N_2, CO_2, and H_2S) calculate $H° - H$ from the Soave, Peng-Robinson, or Lee-Kesler equation. Errors should be less than 4 J/g [14, 62, 80, 89]. The truncated virial equation may be used at low to moderate densities.

For gas mixtures containing nonhydrocarbons, the Lee-Kesler correlation [Eqs. (5-4.1) to (5-4.5) or Tables 5-2 and 5-3] is recommended to estimate $H° - H$. Though errors vary, for nonpolar gas mixtures, differences between calculated and experimental values of $H° - H$ should be only a few joules per gram.

The cubic or truncated virial equations of state are simple to employ and may be useful when extensive iterative calculations must be performed. However, the truncated virial equation can be used only at low or moderate densities.

All the correlations noted above may be used up to the saturated vapor envelope except the truncated virial, which is limited in range to about one-half the critical density. As this envelope is approached, and especially in the critical region, errors are expected to increase. At very high pressures, the correlation of Breedveld and Prausnitz [9] can be used.

Enthalpy departures for pure liquids and liquid mixtures

To estimate the enthalpy departure of pure liquids, it is generally preferable to break the computation into several steps, i.e.,

$$H^L - H° = (H^L - H^{SL}) + (H^{SL} - H^{SV}) + (H^{SV} - H°) \qquad (5\text{-}4.12)$$

where
H^L = liquid enthalpy at T and P
$H°$ = ideal-gas enthalpy at T and $P°$
H^{SL} = saturated liquid enthalpy at T and P_{vp}
H^{SV} = saturated vapor enthalpy at T and P_{vp}

The vapor contribution $H^{SV} - H°$ can be estimated by methods described earlier in this chapter. The term $H^{SL} - H^{SV}$ is simply $-\Delta H_v$, and it can be obtained from enthalpy of vaporization correlations given in Chap. 7. Finally, $H^L - H^{SL}$ represents the effect of pressure on liquid enthalpy. It is normally small relative to the other two terms. The Lee-Kesler correlation [Eqs. (5-4.1) to (5-4.5) or Tables 5-2 and 5-3] may be

applied to the liquid phase and differences taken between $(H° - H)^{SL}$ and $(H° - H)^{SCL}$, where SL and SCL refer to saturated and subcooled liquid.

In the Lee-Kesler method, the enthalpy departure term is $H° - H$, that is, the difference between the enthalpy of the fluid in an ideal-gas state at $P°$ and T and that of the fluid at P, T (liquid or gas). It is not generally recommended that enthalpies of liquids be calculated directly from this difference. The corresponding states methods are usually not sufficiently accurate to estimate ΔH for a phase change. It is preferable to determine phase change ΔH values separately, as indicated in Eq. (5-4.12), and to use other methods for $H^L - H^{SL}$ and $H^{SV} - H°$. (See, however, p. 220.)

When enthalpy departures are desired for liquid mixtures, no completely satisfactory recommendations can be formulated. One method employs a modified form of Eq. (5-4.12). $H^{SV} - H°$ is calculated as described earlier for gas mixtures, and $H^{SL} - H^{SV}$ is set equal to the mole fraction average of the pure component values of $-\Delta H_v$,

$$H^{SL} - H^{SV} = -\sum_j x_j \Delta H_{vj} \tag{5-4.13}$$

Finally, $H^L - H^{SL}$ can be neglected at low pressure, or it can be estimated from Tables 5-2 and 5-3 with pseudocritical constants determined from Eqs. (4-3.1) to (4-3.3), (4-3.4), or (4-6.1) to (4-6.6). This approach is useful only if all components are subcritical. Further, it neglects any heat of mixing in the liquid phase, an assumption which is often warranted unless the liquid phase contains polar components [75].

Good results have been reported when the Soave modification of the Redlich-Kwong equation of state has been used to calculate liquid mixture enthalpy departures for hydrocarbon mixtures not containing hydrogen [89]. This relation is preferred to earlier modified Redlich-Kwong equations [37, 91]. A theoretical equation-of-state method applicable for cryogenic mixtures also is available [58].

If Tables 5-2 and 5-3 are used directly to calculate liquid mixture enthalpy departures, good results are often reported [21, 36, 80, 91].

Mixture enthalpies of vaporization can also be obtained from phase equilibrium measurements [46, 79], but very accurate data are needed to yield reasonable enthalpy values.

To estimate enthalpies (and densities) of hydrocarbon mixtures containing hydrogen, the generalized method of Chueh and Deal [11] is recommended. Huang and Daubert [34] illustrate how one can predict enthalpies of liquid (and vapor) mixtures of petroleum fractions, and Ghormley and Lenoir treat saturated liquid and saturated vapor enthalpies for aliphatic hydrocarbon mixtures [22].

Departure entropies and fugacity coefficients

To estimate departure functions for entropy and fugacity coefficients of pure gases or mixtures, when possible, follow the recommendations made earlier for enthalpies. Table 5-1 may be used for $S - S°$ if an analytical equation of state is selected and $\ln(f/P)$ is determined from Eq. (5-3.11). If the Lee-Kesler method is chosen, use Eqs. (5-4.6) to (5-4.11) or Tables 5-4 to 5-7.

Finally, it should be pointed out that enthalpy departures, entropy departures, and fugacity coefficients are not independent and are related by

$$\frac{H° - H}{RT} = \frac{S° - S}{R} - \ln\frac{f}{P°} \tag{5-4.14}$$

where $P°$ is the pressure in the ideal-gas reference state (see Sec. 5-3).

Example 5-2 Estimate the enthalpy and entropy departures for propylene at 398.15 K and 100 bar. Bier et al. [6] report experimental values as

$$H° - H = 244.58 \text{ J/g} \qquad S° - S = 1.4172 \text{ J/(g·K)}$$

(The ideal-gas reference pressure for entropy $P°$ is 1 bar.)

solution From Appendix A, $M = 42.081$, $T_c = 364.9$ K, $P_c = 46.0$ bar, $Z_c = 0.274$, and $\omega = 0.144$. Thus, $T_r = (398.15)/364.9 = 1.09$ and $P_r = 100/46.0 = 2.17$.
LEE-KESLER METHOD Equations (5-4.4) and (5-4.8), along with Tables 5-2 to 5-5, give

$$\left(\frac{H° - H}{RT_c}\right)^{(0)} = 3.11 \qquad \left(\frac{H° - H}{RT_c}\right)^{(1)} = 1.62$$

$$\left(\frac{S° - S}{R}\right)^{(0)} = 2.18 \qquad \left(\frac{S° - S}{R}\right)^{(1)} = 1.57$$

$$H° - H = \frac{RT_c}{M}\left[\left(\frac{H° - H}{RT_c}\right)^{(0)} + \omega\left(\frac{H° - H}{RT_c}\right)^{(1)}\right]$$

$$= \frac{(8.314)(364.9)}{42.081}[3.11 + (0.144)(1.62)]$$

$$= 241 \text{ J/g}$$

$$S° - S = \frac{R}{M}\left[\left(\frac{S° - S}{R}\right)^{(0)} + \omega\left(\frac{S° - S}{R}\right)^{(1)} - \ln\frac{P°}{P}\right]$$

$$= \frac{8.314}{42.081}\left[2.18 + (0.144)(1.57) - \ln\frac{1}{100}\right]$$

$$= 1.39 \text{ J/(g·K)}$$

The method underpredicts $H° - H$ by 3 J/g and $S° - S$ by 0.03 J/(g·K).
SOAVE EQUATION (3-6.1). From Eq. (5-3.8) and Table 5-1

$$S° - S = -R \ln\frac{Z - B^*}{Z} - R \ln\frac{V}{V°} + \frac{1}{b}\frac{\partial a}{\partial T}\ln\frac{Z}{Z + B^*}$$

TABLE 5-4 Lee-Kesler Residual Entropy [47]

Simple fluid $\left(\dfrac{S^\circ - S}{R}\right)^{(0)}$

T_r	P_r						
	0.010	0.050	0.100	0.200	0.400	0.600	0.800
0.30	11.614	10.008	9.319	8.635	7.961	7.574	7.304
0.35	11.185	9.579	8.890	8.205	7.529	7.140	6.869
0.40	10.802	9.196	8.506	7.821	7.144	6.755	6.483
0.45	10.453	8.847	8.157	7.472	6.794	6.404	6.132
0.50	10.137	8.531	7.841	7.156	6.479	6.089	5.816
0.55	0.038	8.245	7.555	6.870	6.193	5.803	5.531
0.60	0.029	7.983	7.294	6.610	5.933	5.544	5.273
0.65	0.023	0.122	7.052	6.368	5.694	5.306	5.036
0.70	0.018	0.096	0.206	6.140	5.467	5.082	4.814
0.75	0.015	0.078	0.164	5.917	5.248	4.866	4.600
0.80	0.013	0.064	0.134	0.294	5.026	4.649	4.388
0.85	0.011	0.054	0.111	0.239	4.785	4.418	4.166
0.90	0.009	0.046	0.094	0.199	0.463	4.145	3.912
0.93	0.008	0.042	0.085	0.179	0.408	0.750	3.723
0.95	0.008	0.039	0.080	0.168	0.377	0.671	3.556
0.97	0.007	0.037	0.075	0.157	0.350	0.607	1.056
0.98	0.007	0.036	0.073	0.153	0.337	0.580	0.971
0.99	0.007	0.035	0.071	0.148	0.326	0.555	0.903
1.00	0.007	0.034	0.069	0.144	0.315	0.532	0.847
1.01	0.007	0.033	0.067	0.139	0.304	0.510	0.799
1.02	0.006	0.032	0.065	0.135	0.294	0.491	0.757
1.05	0.006	0.030	0.060	0.124	0.267	0.439	0.656
1.10	0.005	0.026	0.053	0.108	0.230	0.371	0.537
1.15	0.005	0.023	0.047	0.096	0.201	0.319	0.452
1.20	0.004	0.021	0.042	0.085	0.177	0.277	0.389
1.30	0.003	0.017	0.033	0.068	0.140	0.217	0.298
1.40	0.003	0.014	0.027	0.056	0.114	0.174	0.237
1.50	0.002	0.011	0.023	0.046	0.094	0.143	0.194
1.60	0.002	0.010	0.019	0.039	0.079	0.120	0.162
1.70	0.002	0.008	0.017	0.033	0.067	0.102	0.137
1.80	0.001	0.007	0.014	0.029	0.058	0.088	0.117
1.90	0.001	0.006	0.013	0.025	0.051	0.076	0.102
2.00	0.001	0.006	0.011	0.022	0.044	0.067	0.089
2.20	0.001	0.004	0.009	0.018	0.035	0.053	0.070
2.40	0.001	0.004	0.007	0.014	0.028	0.042	0.056
2.60	0.001	0.003	0.006	0.012	0.023	0.035	0.046
2.80	0.000	0.002	0.005	0.010	0.020	0.029	0.039
3.00	0.000	0.002	0.004	0.008	0.017	0.025	0.033
3.50	0.000	0.001	0.003	0.006	0.012	0.017	0.023
4.00	0.000	0.001	0.002	0.004	0.009	0.013	0.017

			P_r				
1.000	1.200	1.500	2.000	3.000	5.000	7.000	10.000
7.099	6.935	6.740	6.497	6.182	5.847	5.683	5.578
6.663	6.497	6.299	6.052	5.728	5.376	5.194	5.060
6.275	6.109	5.909	5.660	5.330	4.967	4.772	4.619
5.924	5.757	5.557	5.306	4.974	4.603	4.401	4.234
5.608	5.441	5.240	4.989	4.656	4.282	4.074	3.899
5.324	5.157	4.956	4.706	4.373	3.998	3.788	3.607
5.066	4.900	4.700	4.451	4.120	3.747	3.537	3.353
4.830	4.665	4.467	4.220	3.892	3.523	3.315	3.131
4.610	4.446	4.250	4.007	3.684	3.322	3.117	2.935
4.399	4.238	4.045	3.807	3.491	3.138	2.939	2.761
4.191	4.034	3.846	3.615	3.310	2.970	2.777	2.605
3.976	3.825	3.646	3.425	3.135	2.812	2.629	2.463
3.738	3.599	3.434	3.231	2.964	2.663	2.491	2.334
3.569	3.444	3.295	3.108	2.860	2.577	2.412	2.262
3.433	3.326	3.193	3.023	2.790	2.520	2.362	2.215
3.259	3.188	3.081	2.932	2.719	2.463	2.312	2.170
3.142	3.106	3.019	2.884	2.682	2.436	2.287	2.148
2.972	3.010	2.953	2.835	2.646	2.408	2.263	2.126
2.178	2.893	2.879	2.784	2.609	2.380	2.239	2.105
1.391	2.736	2.798	2.730	2.571	2.352	2.215	2.083
1.225	2.495	2.706	2.673	2.533	2.325	2.191	2.062
0.965	1.523	2.328	2.483	2.415	2.242	2.121	2.001
0.742	1.012	1.557	2.081	2.202	2.104	2.007	1.903
0.607	0.790	1.126	1.649	1.968	1.966	1.897	1.810
0.512	0.651	0.890	1.308	1.727	1.827	1.789	1.722
0.385	0.478	0.628	0.891	1.299	1.554	1.581	1.556
0.303	0.372	0.478	0.663	0.990	1.303	1.386	1.402
0.246	0.299	0.381	0.520	0.777	1.088	1.208	1.260
0.204	0.247	0.312	0.421	0.628	0.913	1.050	1.130
0.172	0.208	0.261	0.350	0.519	0.773	0.915	1.013
0.147	0.177	0.222	0.296	0.438	0.661	0.79	0.908
0.127	0.153	0.191	0.255	0.375	0.570	0.70	0.815
0.111	0.134	0.167	0.221	0.325	0.497	0.62	0.733
0.087	0.105	0.130	0.172	0.251	0.388	0.492	0.599
0.070	0.084	0.104	0.138	0.201	0.311	0.399	0.496
0.058	0.069	0.086	0.113	0.164	0.255	0.329	0.416
0.048	0.058	0.072	0.094	0.137	0.213	0.277	0.353
0.041	0.049	0.061	0.080	0.116	0.181	0.236	0.303
0.029	0.034	0.042	0.056	0.081	0.126	0.166	0.216
0.021	0.025	0.031	0.041	0.059	0.093	0.123	0.162

TABLE 5-5 Lee-Kesler Residual Entropy [47]

Deviation function $\left(\dfrac{S^\circ - S}{R}\right)^{(1)}$

T_r	0.010	0.050	0.100	0.200	0.400	0.600	0.800
				P_r			
0.30	16.782	16.774	16.764	16.744	16.705	16.665	16.626
0.35	15.413	15.408	15.401	15.387	15.359	15.333	15.305
0.40	13.990	13.986	13.981	13.972	13.953	13.934	13.915
0.45	12.564	12.561	12.558	12.551	12.537	12.523	12.509
0.50	11.202	11.200	11.197	11.192	11.182	11.172	11.162
0.55	0.115	9.948	9.946	9.942	9.935	9.928	9.921
0.60	0.078	8.828	8.826	8.823	8.817	8.811	8.806
0.65	0.055	0.309	7.832	7.829	7.824	7.819	7.815
0.70	0.040	0.216	0.491	6.951	6.945	6.941	6.937
0.75	0.029	0.156	0.340	6.173	6.167	6.162	6.158
0.80	0.022	0.116	0.246	0.578	5.475	5.468	5.462
0.85	0.017	0.088	0.183	0.408	4.853	4.841	4.832
0.90	0.013	0.068	0.140	0.301	0.744	4.269	4.249
0.93	0.011	0.058	0.120	0.254	0.593	1.219	3.914
0.95	0.010	0.053	0.109	0.228	0.517	0.961	3.697
0.97	0.010	0.048	0.099	0.206	0.456	0.797	1.570
0.98	0.009	0.046	0.094	0.196	0.429	0.734	1.270
0.99	0.009	0.044	0.090	0.186	0.405	0.680	1.098
1.00	0.008	0.042	0.086	0.177	0.382	0.632	0.977
1.01	0.008	0.040	0.082	0.169	0.361	0.590	0.883
1.02	0.008	0.039	0.078	0.161	0.342	0.552	0.807
1.05	0.007	0.034	0.069	0.140	0.292	0.460	0.642
1.10	0.005	0.028	0.055	0.112	0.229	0.350	0.470
1.15	0.005	0.023	0.045	0.091	0.183	0.275	0.361
1.20	0.004	0.019	0.037	0.075	0.149	0.220	0.286
1.30	0.003	0.013	0.026	0.052	0.102	0.148	0.190
1.40	0.002	0.010	0.019	0.037	0.072	0.104	0.133
1.50	0.001	0.007	0.014	0.027	0.053	0.076	0.097
1.60	0.001	0.005	0.011	0.021	0.040	0.057	0.073
1.70	0.001	0.004	0.008	0.016	0.031	0.044	0.056
1.80	0.001	0.003	0.006	0.013	0.024	0.035	0.044
1.90	0.001	0.003	0.005	0.010	0.019	0.028	0.036
2.00	0.000	0.002	0.004	0.008	0.016	0.023	0.029
2.20	0.000	0.001	0.003	0.006	0.011	0.016	0.021
2.40	0.000	0.001	0.002	0.004	0.008	0.012	0.015
2.60	0.000	0.001	0.002	0.003	0.006	0.009	0.012
2.80	0.000	0.001	0.001	0.003	0.005	0.008	0.010
3.00	0.000	0.001	0.001	0.002	0.004	0.006	0.008
3.50	0.000	0.000	0.001	0.001	0.003	0.004	0.006
4.00	0.000	0.000	0.001	0.001	0.002	0.003	0.005

			P_r				
1.000	1.200	1.500	2.000	3.000	5.000	7.000	10.000
16.586	16.547	16.488	16.390	16.195	15.837	15.468	14.925
15.278	15.251	15.211	15.144	15.011	14.751	14.496	14.153
13.896	13.877	13.849	13.803	13.714	13.541	13.376	13.144
12.496	12.482	12.462	12.430	12.367	12.248	12.145	11.999
11.153	11.143	11.129	11.107	11.063	10.985	10.920	10.836
9.914	9.907	9.897	9.882	9.853	9.806	9.769	9.732
8.799	8.794	8.787	8.777	8.760	8.736	8.723	8.720
7.810	7.807	7.801	7.794	7.784	7.779	7.785	7.811
6.933	6.930	6.926	6.922	6.919	6.929	6.952	7.002
6.155	6.152	6.149	6.147	6.149	6.174	6.213	6.285
5.458	5.455	5.453	5.452	5.461	5.501	5.555	5.648
4.826	4.822	4.820	4.822	4.839	4.898	4.969	5.082
4.238	4.232	4.230	4.236	4.267	4.351	4.442	4.578
3.894	3.885	3.884	3.896	3.941	4.046	4.151	4.300
3.658	3.647	3.648	3.669	3.728	3.851	3.966	4.125
3.406	3.391	3.401	3.437	3.517	3.661	3.788	3.957
3.264	3.247	3.268	3.318	3.412	3.569	3.701	3.875
3.093	3.082	3.126	3.195	3.306	3.477	3.616	3.796
2.399	2.868	2.967	3.067	3.200	3.387	3.532	3.717
1.306	2.513	2.784	2.933	3.094	3.297	3.450	3.640
1.113	1.655	2.557	2.790	2.986	3.209	3.369	3.565
0.820	0.831	1.443	2.283	2.655	2.949	3.134	3.348
0.577	0.640	0.618	1.241	2.067	2.534	2.767	3.013
0.437	0.489	0.502	0.654	1.471	2.138	2.428	2.708
0.343	0.385	0.412	0.447	0.991	1.767	2.115	2.430
0.226	0.254	0.282	0.300	0.481	1.147	1.569	1.944
0.158	0.178	0.200	0.220	0.290	0.730	1.138	1.544
0.115	0.130	0.147	0.166	0.206	0.479	0.823	1.222
0.086	0.098	0.112	0.129	0.159	0.334	0.604	0.969
0.067	0.076	0.087	0.102	0.127	0.248	0.456	0.775
0.053	0.060	0.070	0.083	0.105	0.195	0.355	0.628
0.043	0.049	0.057	0.069	0.089	0.160	0.286	0.518
0.035	0.040	0.048	0.058	0.077	0.136	0.238	0.434
0.025	0.029	0.035	0.043	0.060	0.105	0.178	0.322
0.019	0.022	0.027	0.034	0.048	0.086	0.143	0.254
0.015	0.018	0.021	0.028	0.041	0.074	0.120	0.210
0.012	0.014	0.018	0.023	0.035	0.065	0.104	0.180
0.010	0.012	0.015	0.020	0.031	0.058	0.093	0.158
0.007	0.009	0.011	0.015	0.024	0.046	0.073	0.122
0.006	0.007	0.009	0.012	0.020	0.038	0.060	0.100

TABLE 5-6   Lee-Kesler Fugacity-Pressure Ratio [47]

Simple fluid $\left(\log \dfrac{f}{P}\right)^{(0)}$

T_r	P_r						
	0.010	0.050	0.100	0.200	0.400	0.600	0.800
0.30	-3.708	-4.402	-4.696	-4.985	-5.261	-5.412	-5.512
0.35	-2.471	-3.166	-3.461	-3.751	-4.029	-4.183	-4.285
0.40	-1.566	-2.261	-2.557	-2.848	-3.128	-3.283	-3.387
0.45	-0.879	-1.575	-1.871	-2.162	-2.444	-2.601	-2.707
0.50	-0.344	-1.040	-1.336	-1.628	-1.912	-2.070	-2.177
0.55	-0.008	-0.614	-0.911	-1.204	-1.488	-1.647	-1.755
0.60	-0.007	-0.269	-0.566	-0.859	-1.144	-1.304	-1.413
0.65	-0.005	-0.026	-0.283	-0.576	-0.862	-1.023	-1.132
0.70	-0.004	-0.021	-0.043	-0.341	-0.627	-0.789	-0.899
0.75	-0.003	-0.017	-0.035	-0.144	-0.430	-0.592	-0.703
0.80	-0.003	-0.014	-0.029	-0.059	-0.264	-0.426	-0.537
0.85	-0.002	-0.012	-0.024	-0.049	-0.123	-0.285	-0.396
0.90	-0.002	-0.010	-0.020	-0.041	-0.086	-0.166	-0.276
0.93	-0.002	-0.009	-0.018	-0.037	-0.077	-0.122	-0.214
0.95	-0.002	-0.008	-0.017	-0.035	-0.072	-0.113	-0.176
0.97	-0.002	-0.008	-0.016	-0.033	-0.067	-0.105	-0.148
0.98	-0.002	-0.008	-0.016	-0.032	-0.065	-0.101	-0.142
0.99	-0.001	-0.007	-0.015	-0.031	-0.063	-0.098	-0.137
1.00	-0.001	-0.007	-0.015	-0.030	-0.061	-0.095	-0.132
1.01	-0.001	-0.007	-0.014	-0.029	-0.059	-0.091	-0.127
1.02	-0.001	-0.007	-0.014	-0.028	-0.057	-0.088	-0.122
1.05	-0.001	-0.006	-0.013	-0.025	-0.052	-0.080	-0.110
1.10	-0.001	-0.005	-0.011	-0.022	-0.045	-0.069	-0.093
1.15	-0.001	-0.005	-0.009	-0.019	-0.039	-0.059	-0.080
1.20	-0.001	-0.004	-0.008	-0.017	-0.034	-0.051	-0.069
1.30	-0.001	-0.003	-0.006	-0.013	-0.026	-0.039	-0.052
1.40	-0.001	-0.003	-0.005	-0.010	-0.020	-0.030	-0.040
1.50	-0.000	-0.002	-0.004	-0.008	-0.016	-0.024	-0.032
1.60	-0.000	-0.002	-0.003	-0.006	-0.012	-0.019	-0.025
1.70	-0.000	-0.001	-0.002	-0.005	-0.010	-0.015	-0.020
1.80	-0.000	-0.001	-0.002	-0.004	-0.008	-0.012	-0.015
1.90	-0.000	-0.001	-0.002	-0.003	-0.006	-0.009	-0.012
2.00	-0.000	-0.001	-0.001	-0.002	-0.005	-0.007	-0.009
2.20	-0.000	-0.000	-0.001	-0.001	-0.003	-0.004	-0.005
2.40	-0.000	-0.000	-0.000	-0.001	-0.001	-0.002	-0.003
2.60	-0.000	-0.000	-0.000	-0.000	-0.000	-0.001	-0.001
2.80	0.000	0.000	0.000	0.000	0.000	0.000	0.001
3.00	0.000	0.000	0.000	0.000	0.001	0.001	0.002
3.50	0.000	0.000	0.000	0.001	0.001	0.002	0.003
4.00	0.000	0.000	0.000	0.001	0.002	0.003	0.004

			P_r				
1.000	1.200	1.500	2.000	3.000	5.000	7.000	10.000
-5.584	-5.638	-5.697	-5.759	-5.810	-5.782	-5.679	-5.461
-4.359	-4.416	-4.479	-4.547	-4.611	-4.608	-4.530	-4.352
-3.463	-3.522	-3.588	-3.661	-3.735	-3.752	-3.694	-3.545
-2.785	-2.845	-2.913	-2.990	-3.071	-3.104	-3.063	-2.938
-2.256	-2.317	-2.387	-2.468	-2.555	-2.601	-2.572	-2.468
-1.835	-1.897	-1.969	-2.052	-2.145	-2.201	-2.183	-2.096
-1.494	-1.557	-1.630	-1.715	-1.812	-1.878	-1.869	-1.795
-1.214	-1.278	-1.352	-1.439	-1.539	-1.612	-1.611	-1.549
-0.981	-1.045	-1.120	-1.208	-1.312	-1.391	-1.396	-1.344
-0.785	-0.850	-0.925	-1.015	-1.121	-1.204	-1.215	-1.172
-0.619	-0.685	-0.760	-0.851	-0.958	-1.046	-1.062	-1.026
-0.479	-0.544	-0.620	-0.711	-0.819	-0.911	-0.930	-0.901
-0.359	-0.424	-0.500	-0.591	-0.700	-0.794	-0.817	-0.793
-0.296	-0.361	-0.437	-0.527	-0.637	-0.732	-0.756	-0.735
-0.258	-0.322	-0.398	-0.488	-0.598	-0.693	-0.719	-0.699
-0.223	-0.287	-0.362	-0.452	-0.561	-0.657	-0.683	-0.665
-0.206	-0.270	-0.344	-0.434	-0.543	-0.639	-0.666	-0.649
-0.191	-0.254	-0.328	-0.417	-0.526	-0.622	-0.649	-0.633
-0.176	-0.238	-0.312	-0.401	-0.509	-0.605	-0.633	-0.617
-0.168	-0.224	-0.297	-0.385	-0.493	-0.589	-0.617	-0.602
-0.161	-0.210	-0.282	-0.370	-0.477	-0.573	-0.601	-0.588
-0.143	-0.180	-0.242	-0.327	-0.433	-0.529	-0.557	-0.546
-0.120	-0.148	-0.193	-0.267	-0.368	-0.462	-0.491	-0.482
-0.102	-0.125	-0.160	-0.220	-0.312	-0.403	-0.433	-0.426
-0.088	-0.106	-0.135	-0.184	-0.266	-0.352	-0.382	-0.377
-0.066	-0.080	-0.100	-0.134	-0.195	-0.269	-0.296	-0.293
-0.051	-0.061	-0.076	-0.101	-0.146	-0.205	-0.229	-0.226
-0.039	-0.047	-0.059	-0.077	-0.111	-0.157	-0.176	-0.173
-0.031	-0.037	-0.046	-0.060	-0.085	-0.120	-0.135	-0.129
-0.024	-0.029	-0.036	-0.046	-0.065	-0.092	-0.102	-0.094
-0.019	-0.023	-0.028	-0.036	-0.050	-0.069	-0.075	-0.066
-0.015	-0.018	-0.022	-0.028	-0.038	-0.052	-0.054	-0.043
-0.012	-0.014	-0.017	-0.021	-0.029	-0.037	-0.037	-0.024
-0.007	-0.008	-0.009	-0.012	-0.015	-0.017	-0.012	0.004
-0.003	-0.004	-0.004	-0.005	-0.006	-0.003	0.005	0.024
-0.001	-0.001	-0.001	-0.001	0.001	0.007	0.017	0.037
0.001	0.001	0.002	0.003	0.005	0.014	0.025	0.046
0.002	0.003	0.003	0.005	0.009	0.018	0.031	0.053
0.004	0.005	0.006	0.008	0.013	0.025	0.038	0.061
0.005	0.006	0.007	0.010	0.016	0.028	0.041	0.064

TABLE 5-7   Lee-Kesler Fugacity-Pressure Ratio [47]

Deviation function $\left(\log \dfrac{f}{P}\right)^{(1)}$

T_r	P_r						
	0.010	0.050	0.100	0.200	0.400	0.600	0.800
0.30	-8.778	-8.779	-8.781	-8.785	-8.790	-8.797	-8.804
0.35	-6.528	-6.530	-6.532	-6.536	-6.544	-6.551	-6.559
0.40	-4.912	-4.914	-4.916	-4.919	-4.929	-4.937	-4.945
0.45	-3.726	-3.728	-3.730	-3.734	-3.742	-3.750	-3.758
0.50	-2.838	-2.839	-2.841	-2.845	-2.853	-2.861	-2.869
0.55	-0.013	-2.163	-2.165	-2.169	-2.177	-2.184	-2.192
0.60	-0.009	-1.644	-1.646	-1.650	-1.657	-1.664	-1.671
0.65	-0.006	-0.031	-1.242	-1.245	-1.252	-1.258	-1.265
0.70	-0.004	-0.021	-0.044	-0.927	-0.934	-0.940	-0.946
0.75	-0.003	-0.014	-0.030	-0.675	-0.682	-0.688	-0.694
0.80	-0.002	-0.010	-0.020	-0.043	-0.481	-0.487	-0.493
0.85	-0.001	-0.006	-0.013	-0.028	-0.321	-0.327	-0.332
0.90	-0.001	-0.004	-0.009	-0.018	-0.039	-0.199	-0.204
0.93	-0.001	-0.003	-0.007	-0.013	-0.029	-0.048	-0.141
0.95	-0.001	-0.003	-0.005	-0.011	-0.023	-0.037	-0.103
0.97	-0.000	-0.002	-0.004	-0.009	-0.018	-0.029	-0.042
0.98	-0.000	-0.002	-0.004	-0.008	-0.016	-0.025	-0.035
0.99	-0.000	-0.002	-0.003	-0.007	-0.014	-0.021	-0.030
1.00	-0.000	-0.001	-0.003	-0.006	-0.012	-0.018	-0.025
1.01	-0.000	-0.001	-0.003	-0.005	-0.010	-0.016	-0.021
1.02	-0.000	-0.001	-0.002	-0.004	-0.009	-0.013	-0.017
1.05	-0.000	-0.001	-0.001	-0.002	-0.005	-0.006	-0.007
1.10	-0.000	-0.000	0.000	0.000	0.001	0.002	0.004
1.15	0.000	0.000	0.001	0.002	0.005	0.008	0.011
1.20	0.000	0.001	0.002	0.003	0.007	0.012	0.017
1.30	0.000	0.001	0.003	0.005	0.011	0.017	0.023
1.40	0.000	0.002	0.003	0.006	0.013	0.020	0.027
1.50	0.000	0.002	0.003	0.007	0.014	0.021	0.028
1.60	0.000	0.002	0.003	0.007	0.014	0.021	0.029
1.70	0.000	0.002	0.004	0.007	0.014	0.021	0.029
1.80	0.000	0.002	0.003	0.007	0.014	0.021	0.028
1.90	0.000	0.002	0.003	0.007	0.014	0.021	0.028
2.00	0.000	0.002	0.003	0.007	0.013	0.020	0.027
2.20	0.000	0.002	0.003	0.006	0.013	0.019	0.025
2.40	0.000	0.002	0.003	0.006	0.012	0.018	0.024
2.60	0.000	0.001	0.003	0.006	0.011	0.017	0.023
2.80	0.000	0.001	0.003	0.005	0.011	0.016	0.021
3.00	0.000	0.001	0.003	0.005	0.010	0.015	0.020
3.50	0.000	0.001	0.002	0.004	0.009	0.013	0.018
4.00	0.000	0.001	0.002	0.004	0.008	0.012	0.016

			P_r				
1.000	1.200	1.500	2.000	3.000	5.000	7.000	10.000
-8.811	-8.818	-8.828	-8.845	-8.880	-8.953	-9.022	-9.126
-6.567	-6.575	-6.587	-6.606	-6.645	-6.723	-6.800	-6.919
-4.954	-4.962	-4.974	-4.995	-5.035	-5.115	-5.195	-5.312
-3.766	-3.774	-3.786	-3.806	-3.845	-3.923	-4.001	-4.114
-2.877	-2.884	-2.896	-2.915	-2.953	-3.027	-3.101	-3.208
-2.199	-2.207	-2.218	-2.236	-2.273	-2.342	-2.410	-2.510
-1.677	-1.684	-1.695	-1.712	-1.747	-1.812	-1.875	-1.967
-1.271	-1.278	-1.287	-1.304	-1.336	-1.397	-1.456	-1.539
-0.952	-0.958	-0.967	-0.983	-1.013	-1.070	-1.124	-1.201
-0.700	-0.705	-0.714	-0.728	-0.756	-0.809	-0.858	-0.929
-0.499	-0.504	-0.512	-0.526	-0.551	-0.600	-0.645	-0.709
-0.338	-0.343	-0.351	-0.364	-0.388	-0.432	-0.473	-0.530
-0.210	-0.215	-0.222	-0.234	-0.256	-0.296	-0.333	-0.384
-0.146	-0.151	-0.158	-0.170	-0.190	-0.228	-0.262	-0.310
-0.108	-0.114	-0.121	-0.132	-0.151	-0.187	-0.220	-0.265
-0.075	-0.080	-0.087	-0.097	-0.116	-0.149	-0.180	-0.223
-0.059	-0.064	-0.071	-0.081	-0.099	-0.132	-0.162	-0.203
-0.044	-0.050	-0.056	-0.066	-0.084	-0.115	-0.144	-0.184
-0.031	-0.036	-0.042	-0.052	-0.069	-0.099	-0.127	-0.166
-0.024	-0.024	-0.030	-0.038	-0.054	-0.084	-0.111	-0.149
-0.019	-0.015	-0.018	-0.026	-0.041	-0.069	-0.095	-0.132
-0.007	-0.002	0.008	0.007	-0.005	-0.029	-0.052	-0.085
0.007	0.012	0.025	0.041	0.042	0.026	0.008	-0.019
0.016	0.022	0.034	0.056	0.074	0.069	0.057	0.036
0.023	0.029	0.041	0.064	0.093	0.102	0.096	0.081
0.030	0.038	0.049	0.071	0.109	0.142	0.150	0.148
0.034	0.041	0.053	0.074	0.112	0.161	0.181	0.191
0.036	0.043	0.055	0.074	0.112	0.167	0.197	0.218
0.036	0.043	0.055	0.074	0.110	0.167	0.204	0.234
0.036	0.043	0.054	0.072	0.107	0.165	0.205	0.242
0.035	0.042	0.053	0.070	0.104	0.161	0.203	0.246
0.034	0.041	0.052	0.068	0.101	0.157	0.200	0.246
0.034	0.040	0.050	0.066	0.097	0.152	0.196	0.244
0.032	0.038	0.047	0.062	0.091	0.143	0.186	0.236
0.030	0.036	0.044	0.058	0.086	0.134	0.176	0.227
0.028	0.034	0.042	0.055	0.080	0.127	0.167	0.217
0.027	0.032	0.039	0.052	0.076	0.120	0.158	0.208
0.025	0.030	0.037	0.049	0.072	0.114	0.151	0.199
0.022	0.026	0.033	0.043	0.063	0.101	0.134	0.179
0.020	0.023	0.029	0.038	0.057	0.090	0.121	0.163

$$H° - H = -[A - A° + T(S - S°) + RT(Z - 1)]$$

$$= -\frac{a}{b} \ln \frac{Z}{Z + B^*} + \frac{T}{b} \frac{\partial a}{\partial T} \ln \frac{Z}{Z + B^*} - RT(Z - 1)$$

$$R = 83.14 \text{ cm}^3 \cdot \text{bar}/(\text{mol} \cdot \text{K})$$

$$b = 0.08664 \frac{RT_c}{P_c}$$

$$= \frac{(0.08664)(83.14)(364.9)}{46.0} = 57.14 \text{ cm}^3/\text{mol}$$

$$B^* = \frac{bP}{RT}$$

$$= \frac{(57.14)(100)}{(83.14)(398.15)} = 0.1726$$

$$f\omega = 0.48 + 1.574\omega - 0.176\omega^2$$

$$= 0.703$$

$$a = 0.42748 \frac{[1 + f\omega(1 - T_r^{0.5})]^2 R^2 T_c^2}{P_c}$$

$$= 0.42748 \frac{[1 + 0.703(1 - 1.09^{1/2})]^2(83.14)^2(364.9)^2}{46.0}$$

$$= 8.03 \times 10^6 \text{ bar} \cdot (\text{cm}^3/\text{mol})^2$$

For a pure component,

$$\frac{\partial a}{\partial T} = -Rf\omega \left(\frac{0.42748aT_c}{TP_c} \right)^{1/2}$$

$$= -(83.14)(0.703) \left[\frac{(0.42748)(8.03 \times 10^6)}{(1.09)(46.0)} \right]^{1/2}$$

$$= -15,281 \text{ bar} \cdot (\text{cm}^3/\text{mol})^2/\text{K}$$

If Eq. (3-6.2) is solved for Z, the result is $Z = 0.4470$, $V = 148.0 \text{ cm}^3/\text{mol}$.

$$S° - S = -83.14 \ln \frac{0.4470 - 0.1726}{0.4470} - 83.14 \ln \frac{148.0(1)}{(83.14)(398.15)} - \frac{15,281}{57.14} \ln \frac{0.4470}{0.4470 + 0.1726}$$

$$= 578 \frac{\text{bar} \cdot \text{cm}^3}{\text{mol} \cdot \text{K}}$$

$$S° - S = \frac{578}{42.081} \frac{8.314}{83.14} = 1.37 \text{ J/(g} \cdot \text{K)}$$

$$H° - H = \left[-\frac{8.03 \times 10^6}{56.91} + \frac{398.15}{56.91}(-15,281) \right] \ln \frac{0.447}{0.447 + 0.1726} - (83.14)(398.15)(0.447 - 1)$$

$$= 9.89 \times 10^4 \text{ bar} \cdot \text{cm}^3/\text{mol}$$

$$H° - H = \frac{9.89 \times 10^4}{42.081} \frac{8.314}{83.14} = 235 \text{ J/g}$$

PENG-ROBINSON EQUATION.   For the Peng-Robinson equation, the corresponding equation for $H° - H$ is

$$H° - H = \left(-\frac{a}{2b\sqrt{2}} + \frac{T}{2b\sqrt{2}} \frac{\partial a}{\partial T} \right) \ln \left(\frac{Z - 0.414B^*}{Z + 2.414B^*} \right) - RT(Z - 1)$$

The Peng-Robinson results are

$$S^\circ - S = 1.36 \text{ J/(g·K)}$$
$$H^\circ - H = 235 \text{ J/g}$$

5-5 Heat Capacities of Real Gases

In Chap. 6 we present methods for estimating the heat capacity of pure gases in the ideal-gas state as a function of temperature. Also in this ideal-gas state, for a gas mixture,

$$C_{p_m}^\circ = \sum_i y_i C_{p_i}^\circ \tag{5-5.1}$$

The heat capacity of a real gas is related to the value in the ideal-gas state, at the same temperature and composition:

$$C_p = C_p^\circ + \Delta C_p \tag{5-5.2}$$

where this relation applies to either a pure gas or gas mixture at constant composition. ΔC_p is a residual heat capacity. For a pressure-explicit equation of state, ΔC_p is most conveniently determined by (see p. 159, Ref. 56)

$$\Delta C_p = T \int_\infty^V \left(\frac{\partial^2 P}{\partial T^2} \right) dV - \frac{T(\partial P/\partial T)_V^2}{(\partial P/\partial V)_T} - R \tag{5-5.3}$$

For the Lee-Kesler method

$$C_p - C_p^\circ = \Delta C_p = (\Delta C_p)^{(0)} + \omega (\Delta C_p)^{(1)} \tag{5-5.4}$$

The simple fluid contribution $(\Delta C_p)^{(0)}$ is given in Table 5-8, and the deviation function $(\Delta C_p)^{(1)}$ is given in Table 5-9 as a function of T_r and P_r. If Eq. (5-5.4) and Tables 5-8 and 5-9 are employed for mixtures, the pseudocritical rules given in Eqs. (4-6.3) to (4-6.7) should be used. These rules have been developed primarily from hydrocarbon mixture data, but they should be satisfactory unless highly polar components are present. Tables 5-8 and 5-9 differ somewhat from an earlier correlation by Edmister [17] especially in the critical region, where high accuracy is difficult to achieve in any case.

5-6 True Critical Points of Mixtures

In Chap. 4, emphasis was placed upon the estimation of pseudocritical constants for mixtures. Such constants are necessary if one is to use most corresponding states correlations to estimate mixture PVT or derived properties. However, these pseudocritical constants often differ considerably from the true critical points for mixtures. Estimation techniques

TABLE 5-8 Residual Heat Capacities [47]

Simple fluid $\left(\dfrac{C_p - C_p^{\circ}}{R}\right)^{(0)}$

T_r	P_r 0.010	0.050	0.100	0.200	0.400	0.600	0.800
0.30	2.805	2.807	2.809	2.814	2.830	2.842	2.854
0.35	2.808	2.810	2.812	2.815	2.823	2.835	2.844
0.40	2.925	2.926	2.928	2.933	2.935	2.940	2.945
0.45	2.989	2.990	2.990	2.991	2.993	2.995	2.997
0.50	3.006	3.005	3.004	3.003	3.001	3.000	2.998
0.55	0.118	3.002	3.000	2.997	2.990	2.984	2.978
0.60	0.089	3.009	3.006	2.999	2.986	2.974	2.963
0.65	0.069	0.387	3.047	3.036	3.014	2.993	2.973
0.70	0.054	0.298	0.687	3.138	3.099	3.065	3.033
0.75	0.044	0.236	0.526	3.351	3.284	3.225	3.171
0.80	0.036	0.191	0.415	1.032	3.647	3.537	3.440
0.85	0.030	0.157	0.336	0.794	4.404	4.158	3.957
0.90	0.025	0.131	0.277	0.633	1.858	5.679	5.095
0.93	0.023	0.118	0.249	0.560	1.538	4.208	6.720
0.95	0.021	0.111	0.232	0.518	1.375	3.341	9.316
0.97	0.020	0.104	0.217	0.480	1.240	2.778	9.585
0.98	0.019	0.101	0.210	0.463	1.181	2.563	7.350
0.99	0.019	0.098	0.204	0.447	1.126	2.378	6.038
1.00	0.018	0.095	0.197	0.431	1.076	2.218	5.156
1.01	0.018	0.092	0.191	0.417	1.029	2.076	4.516
1.02	0.017	0.089	0.185	0.403	0.986	1.951	4.025
1.05	0.016	0.082	0.169	0.365	0.872	1.648	3.047
1.10	0.014	0.071	0.147	0.313	0.724	1.297	2.168
1.15	0.012	0.063	0.128	0.271	0.612	1.058	1.670
1.20	0.011	0.055	0.113	0.237	0.525	0.885	1.345
1.30	0.009	0.044	0.089	0.185	0.400	0.651	0.946
1.40	0.007	0.036	0.072	0.149	0.315	0.502	0.711
1.50	0.006	0.029	0.060	0.122	0.255	0.399	0.557
1.60	0.005	0.025	0.050	0.101	0.210	0.326	0.449
1.70	0.004	0.021	0.042	0.086	0.176	0.271	0.371
1.80	0.004	0.018	0.036	0.073	0.150	0.229	0.311
1.90	0.003	0.016	0.031	0.063	0.129	0.196	0.265
2.00	0.003	0.014	0.027	0.055	0.112	0.170	0.229
2.20	0.002	0.011	0.021	0.043	0.086	0.131	0.175
2.40	0.002	0.009	0.017	0.034	0.069	0.104	0.138
2.60	0.001	0.007	0.014	0.028	0.056	0.084	0.112
2.80	0.001	0.006	0.012	0.023	0.046	0.070	0.093
3.00	0.001	0.005	0.010	0.020	0.039	0.058	0.078
3.50	0.001	0.003	0.007	0.013	0.027	0.040	0.053
4.00	0.000	0.002	0.005	0.010	0.019	0.029	0.038

				P_r				
1.000	1.200	1.500	2.000	3.000	5.000	7.000	10.000
2.866	2.878	2.896	2.927	2.989	3.122	3.257	3.466
2.853	2.861	2.875	2.897	2.944	3.042	3.145	3.313
2.951	2.956	2.965	2.979	3.014	3.085	3.164	3.293
2.999	3.002	3.006	3.014	3.032	3.079	3.135	3.232
2.997	2.996	2.995	2.995	2.999	3.019	3.054	3.122
2.973	2.968	2.961	2.951	2.938	2.934	2.947	2.988
2.952	2.942	2.927	2.907	2.874	2.840	2.831	2.847
2.955	2.938	2.914	2.878	2.822	2.753	2.720	2.709
3.003	2.975	2.937	2.881	2.792	2.681	2.621	2.582
3.122	3.076	3.015	2.928	2.795	2.629	2.537	2.469
3.354	3.277	3.176	3.038	2.838	2.601	2.473	2.373
3.790	3.647	3.470	3.240	2.931	2.599	2.427	2.292
4.677	4.359	4.000	3.585	3.096	2.626	2.399	2.227
5.766	5.149	4.533	3.902	3.236	2.657	2.392	2.195
7.127	6.010	5.050	4.180	3.351	2.684	2.391	2.175
10.011	7.451	5.785	4.531	3.486	2.716	2.393	2.159
13.270	8.611	6.279	4.743	3.560	2.733	2.395	2.151
21.948	10.362	6.897	4.983	3.641	2.752	2.398	2.144
******	13.281	7.686	5.255	3.729	2.773	2.401	2.138
22.295	18.967	8.708	5.569	3.821	2.794	2.405	2.131
13.184	31.353	10.062	5.923	3.920	2.816	2.408	2.125
6.458	20.234	16.457	7.296	4.259	2.891	2.425	2.110
3.649	6.510	13.256	9.787	4.927	3.033	2.462	2.093
2.553	3.885	6.985	9.094	5.535	3.186	2.508	2.083
1.951	2.758	4.430	6.911	5.710	3.326	2.555	2.079
1.297	1.711	2.458	3.850	4.793	3.452	2.628	2.077
0.946	1.208	1.650	2.462	3.573	3.282	2.626	2.068
0.728	0.912	1.211	1.747	2.647	2.917	2.525	2.038
0.580	0.719	0.938	1.321	2.016	2.508	2.347	1.978
0.475	0.583	0.752	1.043	1.586	2.128	2.130	1.889
0.397	0.484	0.619	0.848	1.282	1.805	1.907	1.778
0.336	0.409	0.519	0.706	1.060	1.538	1.696	1.656
0.289	0.350	0.443	0.598	0.893	1.320	1.505	1.531
0.220	0.265	0.334	0.446	0.661	0.998	1.191	1.292
0.173	0.208	0.261	0.347	0.510	0.779	0.956	1.086
0.140	0.168	0.210	0.278	0.407	0.624	0.780	0.917
0.116	0.138	0.172	0.227	0.332	0.512	0.647	0.779
0.097	0.116	0.144	0.190	0.277	0.427	0.545	0.668
0.066	0.079	0.098	0.128	0.187	0.289	0.374	0.472
0.048	0.057	0.071	0.093	0.135	0.209	0.272	0.350

TABLE 5-9   Residual Heat Capacities [47]

Deviation function $\left(\dfrac{C_p - C_p^{\circ}}{R}\right)^{(1)}$

T_r	0.010	0.050	0.100	0.200	0.400	0.600	0.800
				P_r			
0.30	8.462	8.445	8.424	8.381	8.281	8.192	8.102
0.35	9.775	9.762	9.746	9.713	9.646	9.568	9.499
0.40	11.494	11.484	11.471	11.438	11.394	11.343	11.291
0.45	12.651	12.643	12.633	12.613	12.573	12.532	12.492
0.50	13.111	13.106	13.099	13.084	13.055	13.025	12.995
0.55	0.511	13.035	13.030	13.021	13.002	12.981	12.961
0.60	0.345	12.679	12.675	12.668	12.653	12.637	12.620
0.65	0.242	1.518	12.148	12.145	12.137	12.128	12.117
0.70	0.174	1.026	2.698	11.557	11.564	11.563	11.559
0.75	0.129	0.726	1.747	10.967	10.995	11.011	11.019
0.80	0.097	0.532	1.212	3.511	10.490	10.536	10.566
0.85	0.075	0.399	0.879	2.247	9.999	10.153	10.245
0.90	0.058	0.306	0.658	1.563	5.486	9.793	10.180
0.93	0.050	0.263	0.560	1.289	3.890	******	10.285
0.95	0.046	0.239	0.505	1.142	3.215	9.389	9.993
0.97	0.042	0.217	0.456	1.018	2.712	6.588	******
0.98	0.040	0.207	0.434	0.962	2.506	5.711	******
0.99	0.038	0.198	0.414	0.911	2.324	5.027	******
1.00	0.037	0.189	0.394	0.863	2.162	4.477	10.511
1.01	0.035	0.181	0.376	0.819	2.016	4.026	8.437
1.02	0.034	0.173	0.359	0.778	1.884	3.648	7.044
1.05	0.030	0.152	0.313	0.669	1.559	2.812	4.679
1.10	0.024	0.123	0.252	0.528	1.174	1.968	2.919
1.15	0.020	0.101	0.205	0.424	0.910	1.460	2.048
1.20	0.016	0.083	0.168	0.345	0.722	1.123	1.527
1.30	0.012	0.058	0.116	0.235	0.476	0.715	0.938
1.40	0.008	0.042	0.083	0.166	0.329	0.484	0.624
1.50	0.006	0.030	0.061	0.120	0.235	0.342	0.437
1.60	0.005	0.023	0.045	0.089	0.173	0.249	0.317
1.70	0.003	0.017	0.034	0.068	0.130	0.187	0.236
1.80	0.003	0.013	0.027	0.052	0.100	0.143	0.180
1.90	0.002	0.011	0.021	0.041	0.078	0.111	0.140
2.00	0.002	0.008	0.017	0.032	0.062	0.088	0.110
2.20	0.001	0.005	0.011	0.021	0.040	0.057	0.072
2.40	0.001	0.004	0.007	0.014	0.028	0.039	0.049
2.60	0.001	0.003	0.005	0.010	0.020	0.028	0.035
2.80	0.000	0.002	0.004	0.008	0.014	0.021	0.026
3.00	0.000	0.001	0.003	0.006	0.011	0.016	0.020
3.50	0.000	0.001	0.002	0.003	0.006	0.009	0.012
4.00	0.000	0.001	0.001	0.002	0.004	0.006	0.008

P_r

1.000	1.200	1.500	2.000	3.000	5.000	7.000	10.000
8.011	7.920	7.785	7.558	7.103	6.270	5.372	4.020
9.430	9.360	9.256	9.080	8.728	8.013	7.290	6.285
11.240	11.188	11.110	10.980	10.709	10.170	9.625	8.803
12.451	12.409	12.347	12.243	12.029	11.592	11.183	10.533
12.964	12.933	12.886	12.805	12.639	12.288	11.946	11.419
12.939	12.917	12.882	12.823	12.695	12.407	12.103	11.673
12.589	12.574	12.550	12.506	12.407	12.165	11.905	11.526
12.105	12.092	12.060	12.026	11.943	11.728	11.494	11.141
11.553	11.536	11.524	11.495	11.416	11.208	10.985	10.661
11.024	11.022	11.013	10.986	10.898	10.677	10.448	10.132
10.583	10.590	10.587	10.556	10.446	10.176	9.917	9.591
10.297	10.321	10.324	10.278	10.111	9.740	9.433	9.075
10.349	10.409	10.401	10.279	9.940	9.389	8.999	8.592
10.769	10.875	10.801	10.523	9.965	9.225	8.766	8.322
11.420	11.607	11.387	10.865	10.055	9.136	8.621	8.152
13.001	******	12.498	11.445	10.215	9.061	8.485	7.986
******	******	******	11.856	10.323	9.037	8.420	7.905
******	******	******	12.388	10.457	9.011	8.359	7.826
******	******	******	13.081	10.617	8.990	8.293	7.747
******	******	******	******	10.805	8.973	8.236	7.670
******	******	******	******	11.024	8.960	8.182	7.595
7.173	2.277	******	******	11.852	8.939	8.018	7.377
3.877	4.002	3.927	******	******	8.933	7.759	7.031
2.587	2.844	2.236	7.716	12.812	8.849	7.504	6.702
1.881	2.095	1.962	2.965	9.494	8.508	7.206	6.384
1.129	1.264	1.327	1.288	3.855	6.758	6.365	5.735
0.743	0.833	0.904	0.905	1.652	4.524	5.193	5.035
0.517	0.580	0.639	0.666	0.907	2.823	3.944	4.289
0.374	0.419	0.466	0.499	0.601	1.755	2.871	3.545
0.278	0.312	0.349	0.380	0.439	1.129	2.060	2.867
0.212	0.238	0.267	0.296	0.337	0.764	1.483	2.287
0.164	0.185	0.209	0.234	0.267	0.545	1.085	1.817
0.130	0.146	0.166	0.187	0.217	0.407	0.812	1.446
0.085	0.096	0.110	0.126	0.150	0.256	0.492	0.941
0.058	0.066	0.076	0.089	0.109	0.180	0.329	0.644
0.042	0.048	0.056	0.066	0.084	0.137	0.239	0.466
0.031	0.036	0.042	0.051	0.067	0.110	0.187	0.356
0.024	0.028	0.033	0.041	0.055	0.092	0.153	0.285
0.015	0.017	0.021	0.026	0.038	0.067	0.108	0.190
0.010	0.012	0.015	0.019	0.029	0.054	0.085	0.146

for the latter can be evaluated by comparison with experimental data. For the former, evaluation is indirect, since the pseudocritical state does not exist in a physical sense.

In this section, we briefly discuss methods of estimating the true critical properties of mixtures. Most techniques are limited to hydrocarbon mixtures or to mixtures of hydrocarbons with CO_2, H_2S, CO, and the permanent gases. A summary of experimental values is given in Ref. 33.

Estimation methods fall into two categories: empirical methods and rigorous methods in which an equation of state is used to solve the Gibbs criteria for a critical point in a mixture. The empirical methods are simpler and are reviewed first.

Mixture critical temperature

The true mixture critical temperature is usually not a linear mole fraction average of the pure component critical temperatures. Li [48] has suggested that if the composition is expressed as

$$\phi_j = \frac{y_j V_{cj}}{\sum_i y_i V_{ci}} \tag{5-6.1}$$

the true mixture critical temperature can be estimated by

$$T_{cT} = \sum_j \phi_j T_{cj} \tag{5-6.2}$$

where y_j = mole fraction of component j
  V_{cj} = critical volume of j
  T_{cj} = critical temperature of j
  T_{cT} = true mixture critical temperature

Chueh and Prausnitz [12] have proposed a similar technique. By defining a *surface fraction* θ_j,

$$\theta_j = \frac{y_j V_{cj}^{2/3}}{\sum_i y_i V_{ci}^{2/3}} \tag{5-6.3}$$

they then relate θ_j and T_{cT} by

$$T_{cT} = \sum_j \theta_j T_{cj} + \sum_i \sum_j \theta_i \theta_j \tau_{ij} \tag{5-6.4}$$

where τ_{ij} is an interaction parameter. τ_{ii} is considered to be zero, and τ_{ij} $(i \neq j)$ can be estimated for several different binary types by

$$\psi_T = A + B \, \delta_T + C \, \delta_T^2 + D \, \delta_T^3 + E \, \delta_T^4 \tag{5-6.5}$$

where $$\psi_T = \frac{2\tau_{ij}}{T_{c_i} + T_{c_j}}$$ (5-6.6)

and $$\delta_T = \left| \frac{T_{c_i} - T_{c_j}}{T_{c_i} + T_{c_j}} \right|$$ (5-6.7)

The coefficients for Eq. (5-6.5) are shown below for a few binary types [73], where $0 \leq \delta_T \leq 0.5$:

Binary	A	B	C	D	E
Containing aromatics	− 0.0219	1.227	− 24.277	147.673	− 259.433
Containing H_2S	− 0.0479	− 5.725	70.974	− 161.319	
Containing CO_2	− 0.0953	2.185	− 33.985	179.068	− 264.522
Containing C_2H_2	− 0.0785	− 2.152	93.084	− 722.676	
Containing CO	− 0.0077	− 0.095	− 0.225	3.528	
All other systems	− 0.0076	0.287	− 1.343	5.443	− 3.038

In Fig. 5-2 the critical temperature of the methane–n-pentane binary is shown plotted as a function of mole fraction, surface fraction, and volume fraction. It is clear that the use of a volume fraction provides essentially a linear relation between ϕ_j and T_{cT}, as predicted by Eq. (5-6.2). When the surface fraction is employed, T_{cT} is slightly nonlinear with θ_j and the interaction term in Eq. (5-6.4) compensates for the nonlinearity.

Spencer et al. [74] reviewed and evaluated a number of proposed methods for estimating true critical temperatures for mixtures. They recommended either the Li or Chueh-Prausnitz correlations described above; 135 binary hydrocarbon mixtures were tested, and the average deviation noted for both methods was less than 4 K. For multicomponent hydro-
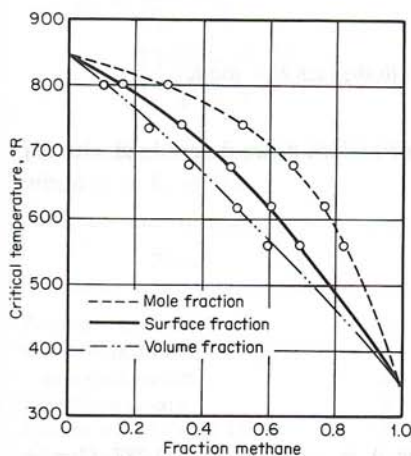
Figure 5-2 Critical temperatures of the methane–n-pentane system as a function of mole fraction, surface fraction, and volume fraction, *(From Ref. 12.)*

carbon systems, larger errors were found (average deviation about 11 K). When hydrocarbon-nonhydrocarbon mixtures were evaluated, the Chueh-Prausnitz method yielded a smaller average deviation [70].

Of the two methods recommended by Spencer et al. [74], the Li relation (5-6.2) is the easier to use, and unless one of the components is a nonhydrocarbon, it is slightly more accurate.

Example 5-3 Estimate the true critical temperature for a mixture of methane, ethane, and n-butane with mole fractions:

$y_{C_1} = 0.193$

$y_{C_2} = 0.470$

$y_{C_4} = \underline{0.337}$

    1.000

Li [48] indicates that the experimental value is 354 K.

solution From Appendix A:

	T_c, K	V_c, cm^3/mol
Methane	190.4	99.2
Ethane	305.4	148.3
n-Butane	425.2	255

LI METHOD. Using Eq. (5-6.1),

	Volume fraction ϕ_i
Methane	0.110
Ethane	0.398
n-Butane	0.492
	1.000

With Eq. (5-6.2)

$$T_{cT} = (0.110)(190.4) + (0.398)(305.4) + (0.492)(425.2) = 352 \text{ K}$$

Deviation = 2 K

CHUEH-PRAUSNITZ METHOD. First, surface fractions θ_j are determined with Eq. (5-6.3):

	Surface fraction θ_j
Methane	0.134
Ethane	0.427
n-Butane	0.439
	1.000

Next, τ_{ij} is found from Eq. (5-6.5) by using $A = -0.0076$, $B = 0.287$, $C = -1.343$, $D = 5.443$, and $E = -3.038$:

i	j	δ_T	ψ_T	τ_{ij}
Methane	Ethane	0.232	0.046	11.4
Methane	n-Butane	0.381	0.144	44.3
Ethane	n-Butane	0.164	0.025	9.1

Then, with Eq. (5-6.4),

$$T_{cT} = (0.134)(190.4) + (0.427)(305.4) + (0.439)(425.2)$$
$$+ (2)(0.134)(0.427)(11.4) + (2)(0.134)(0.439)(44.3)$$
$$+ (2)(0.427)(0.439)(9.1)$$
$$= 353 \text{ K}$$

Deviation $= 1$ K

Mixture critical volumes

Only a few experimental values are available for mixture critical volumes. Thus the range and accuracy of estimation methods are not clearly established. Grieves and Thodos [29] have suggested an approximate graphical method for hydrocarbon mixtures, but an analytical technique by Chueh and Prausnitz [12], modified by Schick and Prausnitz [70], appears to be more accurate. When the surface fraction θ_j is defined as in Eq. (5-6.3), the mixture critical volume is given by a relation analogous to Eq. (5-6.4)

$$V_{cT} = \sum_j \theta_j V_{cj} + \sum_i \sum_j \theta_i \theta_j \nu_{ij} \qquad (5\text{-}6.8)$$

V_{cj} is the critical volume of j, and ν_{ij} is an interaction parameter such that $\nu_{ii} = 0$ and ν_{ij} ($i \neq j$) can be estimated as follows:

$$\psi_v = A + B\delta_v + C\delta_v^2 + D\delta_v^3 + E\delta_v^4 \qquad (5\text{-}6.9)$$

$$\psi_v = \frac{2\nu_{ij}}{V_{ci} + V_{cj}} \qquad (5\text{-}6.10)$$

$$\delta_v = \left| \frac{V_{ci}^{2/3} - V_{cj}^{2/3}}{V_{ci}^{2/3} + V_{cj}^{2/3}} \right| \qquad (5\text{-}6.11)$$

The coefficients for Eq. (5-6.9) are given below for a few binary types [73] when $0 \leq \delta_v \leq 0.5$.

Binary	A	B	C	D	E
Aromatic-aromatic	0	0	0	0	0
Containing at least one cycloparaffin	0	0	0	0	0
Paraffin-aromatic	0.0753	-3.332	2.220	0	0
System with CO_2 or H_2S	-0.4957	17.1185	-168.56	587.05	-698.89
All other systems	0.1397	-2.9672	1.8337	-1.536	0

Spencer et al. [74] evaluated Eq. (5-6.8) for 23 binary hydrocarbon mixtures *and 8 binaries consisting of a hydrocarbon and a nonhydrocarbon*. They report an average error of 10.5 percent, with particularly poor results for ethane-cyclohexane, ethylene-propylene, and several of the systems containing nonhydrocarbons. However, this large error may in part be explained by experimental inaccuracies. It is much more difficult to measure V_{cT} than to measure T_{cT} or P_{cT}. Spencer et al. [74] note that, when V_{cT} is correlated by

$$V_{cT} = y_1 V_{c_1} + y_2 V_{c_2} + V_c^{EX} \qquad (5\text{-}6.12)$$

for a binary of 1 and 2, V_c^{EX} values for some systems are positive and for others are negative. No generalized methods are available to estimate either the sign or the magnitude.

Example 5-4 Estimate the true critical volume of a mixture of toluene and *n*-hexane containing 50.5 mole percent *n*-hexane. The experimental value is 325 cm³/mol [88].

solution Equation (5-6.8) will be used. From Appendix A, V_c (*n*-hexane) = 370 cm³/mol and V_c (toluene) = 316 cm³/mol. Thus with Eq. (5-6.3),

$$\theta_{n\text{-}C_6} = \frac{(0.505)(370^{2/3})}{(0.505)(370^{2/3}) + (0.495)(316^{2/3})} = 0.531$$

$$\theta_{tol} = 0.469$$

With Eq. (5-6.11)

$$\delta_v = \left| \frac{370^{2/3} - 316^{2/3}}{370^{2/3} + 316^{2/3}} \right| = 0.0525$$

Then with Eq. (5-6.9),

$$\psi_v = A + B\delta_v + C\delta_v^2 + D\delta_v^3 + E\delta_v^4$$
$$= 0.0753 + (-3.332)(0.0525) + (2.220)(0.0525)^2$$
$$= -0.094$$
$$= \frac{2\nu_{12}}{370 + 316}$$
$$\nu_{12} = -32$$

Then, with Eq. (5-6.8),

$$V_{cT} = (0.531)(370) + (0.469)(316) + (2)(-32)(0.531)(0.469)$$
$$= 328 \text{ cm}^3/\text{mol}$$

$$\text{Error} = \frac{328 - 325}{325} \times 100 = 1\%$$

Mixture critical pressure

The dependence of mixture critical pressures on mole fraction is often nonlinear, and estimation of P_{cT} is often unreliable. Two approaches are illustrated below.

Kreglewski and Kay [45] derived an approximate expression for P_{cT} by using conformal solution theory. T_{cT} is required in the calculation, and Kreglewski and Kay also suggest how this property may be determined. However, Spencer et al. [74] found better results in determining P_{cT} if T_{cT} is found from Eq. (5-6.2). To find P_{cT}, the liquid molal volumes for each component at $T_r = 0.6$, V_i^*, must first be obtained. Kreglewski [44] tabulates this volume for many pure liquids; alternatively, it can be estimated by methods presented in Chap. 3. The sequential set of equations to employ then follow for a binary of 1 and 2:

$$V_{12}^* = \frac{[(V_1^*)^{1/3} + (V_2^*)^{1/3}]^3}{8} \tag{5-6.13}$$

$$V^* = V_1^* y_1 + V_2^* y_2 + (2V_{12}^* - V_1^* - V_2^*) y_1 y_2 \tag{5-6.14}$$

where y_1 and y_2 are mole fractions. Next, *surface* fractions are defined as

$$\theta_1 = \frac{y_1 V_1^{*2/3}}{y_1 V_1^{*2/3} + y_2 V_2^{*2/3}} \tag{5-6.15}$$

$$\theta_2 = 1 - \theta_1 \tag{5-6.16}$$

$$T_{12}^* = \frac{2V_{12}^{*1/3}}{V_1^{*1/3}/T_{c1} + V_2^{*1/3}/T_{c2}} \tag{5-6.17}$$

$$T^* = V^{*1/3} \left[\frac{T_{c1}\theta_1}{V_1^{*1/3}} + \frac{T_{c2}\theta_2}{V_2^{*1/3}} + \left(\frac{2T_{12}^*}{V_{12}^{*1/3}} - \frac{T_{c1}}{V_1^{*1/3}} - \frac{T_{c2}}{V_2^{*1/3}} \right) \theta_1\theta_2 \right] \tag{5-6.18}$$

$$\omega_{12} = \frac{2}{1/\omega_1 + 1/\omega_2} \tag{5-6.19}$$

$$\omega = \omega_1\theta_1 + \omega_2\theta_2 + (2\omega_{12} - \omega_1 - \omega_2)\theta_1\theta_2 \tag{5-6.20}$$

where ω is the acentric factor. Finally,

$$P^* = \frac{T^*}{V^{*1/3}} \frac{P_{c1}\theta_1 + P_{c2}\theta_2}{T_{c1}\theta_1/V_1^{*1/3} + T_{c2}\theta_2/V_2^{*1/3}} \tag{5-6.21}$$

and

$$P_{cT} = P^* \left[1 + (5.808 + 4.93\omega) \left(\frac{T_{cT}}{T^*} - 1 \right) \right] \tag{5-6.22}$$

with T_{cT} from Eq. (5-6.2) as noted before.

Spencer et al. [73, 74] evaluated this approach and found an average deviation of about 1 bar when calculated values of P_{cT} were compared against experimental data; 967 mixture data points were tested. Methane systems were not included, because all available correlations give significant error for such mixtures. The method is illustrated in Example 5-5. In most cases, Eq. (5-6.22) can be simplified by approximating P^*, T^*, and ω by mole fraction averages of the pure component properties P_{ci}, T_{ci}, and ω_i [40, 73, 74]. Average errors increase to only about 1.3 bar.

Example 5-5 Estimate the critical pressure for a mixture of ethane and benzene which contains 39.2 mole percent ethane. The true critical pressure and temperature are reported to be 84.96 bar and 499.0 K [39].

solution Properties of the pure components from Appendix A are:

Property	Ethane	Benzene
T_c, K	305.4	562.2
P_c, bar	48.8	48.9
ω	0.099	0.212
V_c, cm^3/mol	148.3	259

From Kreglewski [44] V^* (ethane) = 54.87 cm^3/mol and V^* (benzene) = 93.97 cm^3/mol. Following Eqs. (5-6.13) to (5-6.21), with ethane = 1 and benzene = 2, we have

$$V_{12}^* = \frac{[(54.87)^{1/3} + (93.97)^{1/3}]^3}{8} = 72.7 \ cm^3/mol$$

$$V^* = (54.87)(0.392) + (93.97)(0.608) + [(2)(72.7) - 54.87$$
$$- 93.97](0.392)(0.608) = 77.8 \ cm^3/mol$$

$$\theta_1 = \frac{(0.392)(54.87)^{2/3}}{(0.392)(54.87)^{2/3} + (0.608)(93.97)^{2/3}} = 0.310$$

$$\theta_2 = 1 - 0.310 = 0.690$$

$$T_{12}^* = \frac{(2)(72.7)^{1/3}}{(54.87)^{1/3}/305.4 + (93.97)^{1/3}/562.2} = 406 \ K$$

$$T^* = (77.8)^{1/3} \left\{ \frac{(305.4)(0.310)}{(54.87)^{1/3}} + \frac{(562.2)(0.690)}{(93.97)^{1/3}} \right.$$
$$+ \left[\frac{(2)(406)}{(72.7)^{1/3}} - \frac{305.4}{(54.87)^{1/3}} - \frac{562.2}{(93.97)^{1/3}} \right] (0.310)(0.690) \right\}$$
$$= 462 \ K$$

$$\omega_{12} = \frac{2}{1/0.099 + 1/0.212} = 0.135$$

$$\omega = (0.099)(0.310) + (0.212)(0.690) + [(2)(0.135)$$
$$- 0.099 - 0.212](0.310)(0.690)$$
$$= 0.168$$

$$P^* = \frac{462}{(77.8)^{1/3}} \frac{(488)(0.310) + (489)(0.690)}{\dfrac{(305.4)(0.310)}{(54.87)^{1/3}} + \dfrac{(562.2)(0.690)}{(93.97)^{1/3}}}$$
$$= 48.0 \ bar$$

Before using Eq. (5-6.22), T_{cT} must be estimated. With Eqs. (5-6.1) and (5-6.2),

$$\theta_1 = \frac{(0.392)(148.3)}{(0.392)(148.3) + (0.608)(259)} = 0.270$$

$$T_{cT} = (0.270)(305.4) + (0.730)(562.2) = 493 \ K$$

Then, with Eq. (5-6.22),

$$P_{cT} = 48.0 \left\{ 1 + [5.808 + (4.93)(0.168)] \left(\frac{493}{462} - 1 \right) \right\} = 69.4 \text{ bar}$$

$$\text{Error} = \frac{69.4 - 83.8}{83.8} \times 100 = -18\%$$

Spencer et al. [73] report an average deviation of -13 percent when the Kreglewski and Kay method is applied to this very nonlinear system. Tests in most other systems led to much less error.

An alternate method for predicting the critical pressures for mixtures was developed by Chueh and Prausnitz [12]. P_{cm} was related to T_{cm} and V_{cm} by a modified Redlich-Kwong equation of state (see Secs. 3-6 and 4-5).

$$P_{cT} = \frac{RT_{cT}}{V_{cT} - b_m} - \frac{a_m}{T_{cT}^{1/2} V_{cT}(V_{cT} + b_m)} \tag{5-6.23}$$

where T_{cT} and V_{cT} are calculated from methods described earlier in this section. The mixture coefficients for determining P_{cT} are defined as

$$b_m = \sum_j y_j b_j = \sum_j \frac{y_j \Omega_{b_j}^* R T_{cj}}{P_{cj}} \tag{5-6.24}$$

$$a_m = \sum_i \sum_j y_i y_j a_{ij} \tag{5-6.25}$$

with
$$\Omega_{b_j}^* = 0.0867 - 0.0125\omega_j + 0.011\omega_j^2 \tag{5-6.26}$$

$$a_{ii} = \frac{\Omega_{a_i}^* R^2 T_{ci}^{2.5}}{P_{ci}} \tag{5-6.27}$$

$$a_{ij} = \frac{(\Omega_{a_i}^* + \Omega_{a_j}^*) R T_{cij}^{1.5}(V_{ci} + V_{cj})}{4[0.291 - 0.04(\omega_i + \omega_j)]} \tag{5-6.28}$$

$$T_{cij} = (1 - k_{ij}) \sqrt{T_{ci} T_{cj}} \tag{5-6.29}$$

$$\Omega_{a_j}^* = \left(\frac{RT_{cj}}{V_{cj} - b_j} - P_{cj} \right) \frac{P_{cj} V_{cj}(V_{cj} + b_j)}{(RT_{cj})^2} \tag{5-6.30}$$

The interaction parameter k_{ij} usually ranges from 0.1 to 0.01. Values for a large number of binary systems have been tabulated [12].

Spencer et al. [74] have reported that the average deviation between P_{cT} estimated from the Chueh-Prausnitz correlation and experimental values was 2 bar unless methane was one of the components. In such cases, the deviation was often much larger. Other techniques for estimating P_{cm} for systems containing methane have been suggested [2, 29, 77], but they either are limited to aliphatic hydrocarbons or are graphical with a trial-and-error solution. A method developed by Teja et al. [83] gave very large errors in some cases.

Example 5-6 Repeat Example 5-5 by using the Chueh-Prausnitz method to estimate P_{cT}.

solution The properties of pure ethane and benzene are given in Example 5-5. Using the Chueh-Prausnitz methods to calculate T_{cT} and V_{cT} for this mixture gives $T_{cT} = 493$ K and $V_{cT} = 185$ cm^3/mol; $k_{12} = 0.03$ for this binary [12]. Then

$$\Omega_{b1}^* = 0.0867 - (0.0125)(0.099) + (0.011)(0.099)^2 = 0.0856$$

$$\Omega_{b2}^* = 0.0846$$

$$b_1 = \frac{(0.0856)(83.14)(305.4)}{48.8} = 44.52 \text{ cm}^3/\text{mol}$$

$$b_2 = 80.87 \text{ cm}^3/\text{mol}$$

$$b_m = (0.392)(44.52) + (0.608)(80.87) = 66.62 \text{ cm}^3/\text{mol}$$

$$\Omega_{a1}^* = \left(\frac{RT_{c1}}{V_{c1} - b_1} - P_{c1}\right)\frac{P_{c1}V_{c1}(V_{c1} + b_1)}{(RT_{c1})^2}$$

$$= \left[\frac{(83.14)(305.4)}{148.3 - 44.52} - 48.8\right]\left\{\frac{(48.8)(148.3)(148.3 + 44.52)}{[(83.14)(305.4)]^2}\right\}$$

$$= 0.424$$

$$\Omega_{a2}^* = 0.421$$

$$a_1 = \frac{\Omega_{a1}R^2T_{c1}^{2.5}}{P_{c1}} = \frac{(0.424)(83.14)^2(305.4)^{2.5}}{48.8}$$

$$= 97.88 \times 10^6 \text{ cm}^6 \cdot \text{bar} \cdot \text{K}^{0.5}/\text{mol}^2$$

$$a_2 = 446.0 \times 10^6 \text{ cm}^6 \cdot \text{bar} \cdot \text{K}^{0.5}/\text{mol}^2$$

$$T_{c12} = [(305.4)(562.2)]^{1/2}(1 - 0.03) = 401.9 \text{ K}$$

$$a_{12} = \frac{(\tfrac{1}{4})(0.424 + 0.421)(83.14)(401.9)^{1.5}(148.3 + 259)}{0.291 - (0.04)(0.099 + 0.212)}$$

$$= 206.9 \times 10^6 \text{ cm}^6 \cdot \text{bar} \cdot \text{K}^{0.5}/\text{mol}^2$$

$$a_m = 10^6 [(0.392)^2(97.88) + (0.608)^2(446.0) + (2)(0.392)(0.608)(206.9)]$$

$$= 278.5 \times 10^6 \text{ cm}^6 \cdot \text{bar} \cdot \text{K}^{0.5}/\text{mol}^2$$

Then
$$P_{cT} = \frac{RT_{cT}}{V_{cT} - b_m} - \frac{a_m}{T_{cT}^{1/2}V_{cT}(V_{cT} + b_m)}$$

$$= \frac{(83.14)(493)}{185 - 66.62} - \frac{278.5 \times 10^6}{(493)^{1/2}(185)(185 + 66.62)}$$

$$= 76.8 \text{ bar}$$

$$\text{Error} = \frac{76.8 - 84.9}{84.9} \times 100 = -10\%$$

Rigorous methods

The Gibbs criteria for the true critical point of a mixture with n components may be expressed in various forms, but the most convenient (see pp. 250 and 251, Ref. 56) when using a pressure explicit equation of state is

$$L = \begin{vmatrix} A_{11} & A_{12} \dots A_{1n} \\ A_{21} & A_{22} \\ \vdots \\ A_{n1} & \dots \dots A_{nn} \end{vmatrix} = 0 \tag{5-6.31}$$

$$M = \begin{vmatrix} A_{11} & A_{12} \dots A_{1n} \\ A_{21} & A_{22} \\ \vdots \\ A_{n-1,1} & \dots A_{n-1,n} \\ \dfrac{\partial L}{\partial N_1} & \dots & \dfrac{\partial L}{\partial N_n} \end{vmatrix} = 0 \tag{5-6.32}$$

where

$$A_{12} = \left(\frac{\partial^2 A}{\partial N_1 \partial N_2}\right)_{T,\underline{V}} \tag{5-6.33}$$

Thus, all the A terms in Eqs. (5-6.31) and (5-6.32) are second derivatives of the total Helmholtz energy $\underline{A}$ with respect to moles at constant temperature and total volume $\underline{V}$. The determinants expressed by Eqs. (5-6.31) and (5-6.32) are solved simultaneously for the critical volume and critical temperature. The critical pressure is then found from the original equation of state. Peng and Robinson [61] used their equation of state to calculate mixture critical points; later Heidemann and Khalil [32], Michelsen and Heidemann [54], and Michelsen [53] used the Soave equation. Both of these equations of state gave more accurate estimates for critical temperatures and pressures than did the other empirical methods in this section. For example, the Soave equation predicts a critical pressure of 83.9 bar for the mixture in Example 5-5 for an error of only 0.1 percent. These equations of state should not be used for the prediction of critical volumes.

Recommendations

To estimate the true critical temperature and pressure of a mixture, use Eqs. (5-6.31) and (5-6.32) along with either the Soave or the Peng-Robinson equation. Heidemann's [32, 54] method for solving these equations is particularly efficient, but it must still be carried out on a computer. For more rapid estimates of the true critical temperature of a hydrocarbon mixture, use the method of Li [Eq. (5-6.2)]. If the mixture contains non-hydrocarbons, the Chueh-Prausnitz correlation is preferred [Eq. (5-6.4)], although the interaction parameter τ_{ij} can be evaluated only for relatively simple binary pairs. For rapid estimates of the true critical pressure of a mixture, either the Kreglewski-Kay or the Chueh-Prausnitz method may be used. Neither is particularly applicable for systems containing meth-

ane. Errors found are usually considerably larger for P_{cT} estimations than for T_{cT}.

To estimate the true critical volume of a mixture, Eq. (5-6.8) is recommended. However, as above, the interaction parameter ν_{ij} can be determined for only a limited number of binary types. The Soave and Peng-Robinson equations do not give accurate estimates of mixture critical volumes.

The empirical methods in this section have been developed and tested primarily with hydrocarbon mixtures. When these estimation methods are applied to nonhydrocarbon mixtures, no reliable estimate of the error can be given.

5-7 Heat Capacities of Liquids

There are three liquid heat capacities in common use: C_{pL}, $C_{\sigma L}$, and $C_{\text{sat}L}$. The first represents the change in enthalpy with temperature at constant pressure; the second shows the variation in enthalpy of a saturated liquid with temperature; the third indicates the energy required to effect a temperature change while maintaining the liquid in a saturated state. The three heat capacities are related as follows:

$$C_{\sigma L} = \frac{dH_{\sigma L}}{dT} = C_{pL} + \left[V_{\sigma L} - T\left(\frac{\partial V}{\partial T}\right)_p \right]\left(\frac{dP}{dT}\right)_{\sigma L}$$
$$= C_{\text{sat}L} + V_{\sigma L}\left(\frac{dP}{dT}\right)_{\sigma L} \tag{5-7.1}$$

The term $(dP/dT)_{\sigma L}$ represents the change in vapor pressure with temperature. Except at high reduced temperatures, all three forms of the liquid heat capacity are in close numerical agreement. Most estimation techniques yield either C_{pL} or $C_{\sigma L}$, although $C_{\text{sat}L}$ is often the quantity measured experimentally.

Liquid heat capacities are not strong functions of temperature except above $T_r = 0.7$ to 0.8. In fact, a shallow minimum is often reported at temperatures slightly below the normal boiling point. At high reduced temperatures, liquid heat capacities are large and are strong functions of temperature. The general trend is illustrated in Fig. 5-3 for propylene.

Near the normal boiling point, most liquid organic compounds have heat capacities between 1.2 and 2 J/(g·K). In this temperature range, there is essentially no effect of pressure [20].

Experimentally reported liquid heat capacities of hydrocarbons have been correlated in a nomograph [20] and expressed in analytical form [30, 31, 78]. A tabulation of available data is given by San José [69].

Estimation methods applicable for liquid heat capacities fall into four general categories: theoretical, group contribution, corresponding states, and Watson's thermodynamic cycle [65, 87]. Group contribution and cor-
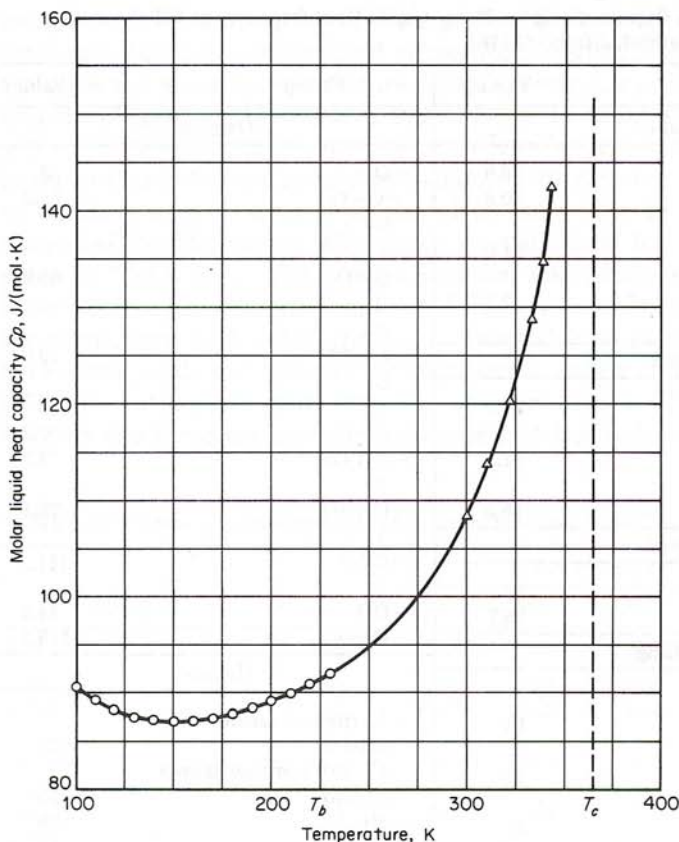
Figure 5-3 Heat capacity of liquid propylene. o, Ref. 63; Δ, Ref. 5.

responding states methods are described below, and recommendations are presented at the end of the section. Theoretical methods are based on the estimation of liquid heat capacities at constant volume by considering each mode of energy storage separately. Reliable estimation procedures have not yet been developed for engineering use, although Bondi [7, 8], for high-molecular-weight liquids and polymers, has suggested some useful approximations that are particularly valuable. A similar, earlier treatment was published by Sakiadis and Coates [68]. Ogiwara et al. [57] have given a group contribution method for constant-volume liquid heat capacities.

Group contribution methods

The assumption is made that various groups in a molecule contribute a definite value to the total molar heat capacity that is independent of other

TABLE 5-10 Group Contributions for Molar Liquid Heat Capacity at 293 K for the Chueh-Swanson Method, J/(mol·K) [10]

Group	Value†	Group	Value†
Alkane		**Oxygen**	
$-CH_3$	36.8	$-O-$	35
$-CH_2-$	30.4	$>C=O$	53.0
$-CH-$	21.0	$\begin{array}{c}H\\|\\-C=O\end{array}$	53.0
$-C-$	7.36	$\begin{array}{c}O\\||\\-C-OH\end{array}$	79.9
Olefin			
$=CH_2$	21.8	$\begin{array}{c}O\\||\\-C-O-\end{array}$	60.7
$=C-H$	21.3	$-CH_2OH$	73.2
$=C-$	15.9	$-CHOH$	76.1
Alkyne		$-COH$	111.3
$\equiv C-H$	24.7	$-OH$	44.8
$-C\equiv$	24.7	$-ONO_2$	119.2
In a Ring		**Halogen**	
$-CH-$	18	$-Cl$ (first or second on a carbon)	36
$-C=$ or $-C-$	12	$-Cl$ (third or fourth on a carbon)	25
$-CH=$	22	$-Br$	38
$-CH_2-$	26	$-F$	17
Nitrogen		$-I$	36
$\begin{array}{c}H\\|\\H-N-\\|\\H\end{array}$	58.6	**Sulfur**	
		$-SH$	44.8
		$-S-$	33
$-N-$	43.9	**Hydrogen**	
$-N-$	31	H— (for formic acid, formates, hydrogen cyanide, etc.)	15
$-N=$ (in a ring)	19		
$-C\equiv N$	58.2		

†Add 18.8 for any carbon group which fulfills the following criterion: a carbon group which is joined by a single bond to a carbon group connected by a double or triple bond with a third carbon group. In some cases a carbon group fulfills the above criterion in more ways than one. In these cases 18.8 should be added each time the group fulfills the criterion. The following are exceptions to the 18.8 addition rule:

1. No 18.8 additions for $-CH_3$ groups.

2. For a $-CH_2-$ group fulfilling the 18.8 addition criterion, add 10.5 instead of 18.8. However, when the $-CH_2-$ group fulfills the addition criterion in more ways than one, the addition should be 10.5 the first time and 18.8 for each subsequent addition. (See Example 5-7.)

3. No 18.8 addition for any carbon group in a ring.

groups present. Johnson and Huang [38], Shaw [72], and Chueh and Swanson [10] have all proposed values for different molecular groups to estimate C_{pL} at room temperature. Shaw's method is applicable at 298 K, and the others are to be used at 293 K. Both the Shaw and Chueh-Swanson methods are accurate, but the latter is more general; group contributions for this technique are shown in Table 5-10. Another additive method in which structural increments are given from -25 to $100°C$ has been suggested by Missenard [55]; group contributions for this scheme are given in Table 5-11. The Chueh-Swanson and Missenard methods are illustrated in Examples 5-7 and 5-8. Missenard's method cannot be used for compounds with double bonds, nor should it be used if the temperature corresponds to a reduced temperature in excess of 0.75. When $T_r <$ 0.75, the estimated value may be considered to be C_{pL}, $C_{\sigma L}$, or C_{satL}, because the three are essentially identical at low reduced temperatures.

TABLE 5-11   Group Contributions for Missenard Method, J/(mol·K) [55]

Group	Temperature, K					
	248	273	298	323	348	373
$-H$	12.5	13.4	14.6	15.5	16.7	18.8
$-CH_3$	38.5	40.0	41.6	43.5	45.8	48.3
$-CH_2-$	27.2	27.6	28.2	29.1	29.9	31.0
$-CH-$	20.9	23.8	24.9	25.7	26.6	28.0
$-C-$	8.4	8.4	8.4	8.4	8.4	
$-C\equiv C-$	46.0	46.0	46.0	46.0		
$-O-$	28.9	29.3	29.7	30.1	30.5	31.0
$-CO-$ (ketone)	41.8	42.7	43.5	44.4	45.2	46.0
$-OH$	27.2	33.5	43.9	52.3	61.7	71.1
$-COO-$ (ester)	56.5	57.7	59.0	61.1	63.2	64.9
$-COOH$	71.1	74.1	78.7	83.7	90.0	94.1
$-NH_2$	58.6	58.6	62.8	66.9		
$-NH-$	51.0	51.0	51.0			
$-N-$	8.4	8.4	8.4			
$-CN$	56.1	56.5	56.9			
$-NO_2$	64.4	64.9	65.7	66.9	68.2	
$-NH-NH-$	79.5	79.5	79.5			
C_6H_5- (phenyl)	108.8	113.0	117.2	123.4	129.7	136.0
$C_{10}H_7-$ (naphthyl)	179.9	184.1	188.3	196.6	205.	213.
$-F$	24.3	24.3	25.1	25.9	27.0	28.2
$-Cl$	28.9	29.3	29.7	30.1	30.8	31.4
$-Br$	35.1	35.6	36.0	36.4	37.2	38.1
$-I$	39.3	39.7	40.4	41.0		
$-S-$	37.2	37.7	38.5	39.3		

Errors for the Chueh-Swanson method rarely exceed 2 to 3 percent and those for Missenard's method ± 5 percent.

Example 5-7 Estimate the liquid heat capacity of 1,4-pentadiene at 20°C by using the Chueh-Swanson group contribution method.

solution From Table 5-10

$$C_{pL}\ (20°C) = 2(CH_2=) + 2(-CH=) + -CH_2^- + \text{corrections noted in Table 5-10}$$

$$= (2)(21.8) + (2)(21.3) + 30.4 + 10.5 + 18.8$$

$$= 146 \text{ J/(mol·K)}$$

Tamplin and Zuzic [78] indicate that $C_{pL} = 147$ J/(mol·K) at 293 K.

Example 5-8 By using Missenard's group contribution method, estimate the liquid heat capacity of isopropyl alcohol at 273 K.

solution With Table 5-11

$$C_{pL}\ (0°C) = 2(-CH_3) + -\overset{|}{\underset{|}{C}}H + -OH$$

$$= (2)(40.0) + 23.8 + 33.5$$

$$= 137.2 \text{ J/(mol·K)}$$

The experimental value is 135.8 J/(mol·K) [25].

Corresponding states methods

Several corresponding states methods for liquid heat capacity estimation have been cast in the form of Eq. (5-5.4). For example, with Tables 5-8 and 5-9, one can estimate the heat capacity departure function $C_{pL} - C_p^\circ$ for liquids as well as for gases. Good results have also been reported by using an analytical form of the Lee-Kesler heat capacity departure function [47] for calculating liquid heat capacities for hydrocarbons [13]. Bondi [7] has reviewed many forms. A modification† of one of his equations that was suggested originally by Rowlinson [66] is

$$\frac{C_{pL} - C_p^\circ}{R} = 1.45 + 0.45(1 - T_r)^{-1} + 0.25\omega[17.11 \qquad (5\text{-}7.2)$$
$$+ 25.2(1 - T_r)^{1/3}T_r^{-1} + 1.742(1 - T_r)^{-1}]$$

C_{pL}, $C_{\sigma L}$, and C_{satL} can also be related to each other by the approximate corresponding states relations

$$\frac{C_{pL} - C_{\sigma L}}{R} = \exp(20.1T_r - 17.9) \qquad (5\text{-}7.3)$$

and

$$\frac{C_{\sigma L} - C_{satL}}{R} = \exp(8.655T_r - 8.385) \qquad (5\text{-}7.4)$$

---

†This equation has been given incorrectly in Refs. 7, 8, 64, and 81.

Equations (5-7.3) and (5-7.4) are valid for $T_r < 0.99$. Below $T_r \sim 0.8$, $C_{\sigma L}$, C_{pL}, and $C_{\text{sat}L}$ may be considered to be the same number.

Example 5-9 Estimate the liquid heat capacity of cis-2-butene at 349.8 K by using the Rowlinson-Bondi corresponding states correlation.

solution From Appendix A, $T_c = 435.6$ K and $\omega = 0.202$. From [76], $C_p^\circ = 91.00$ J/(mol·K). The reduced temperature is 349.8/435.6 = 0.803. Equation (5-7.2) gives

$$\frac{C_{pL} - C_p^\circ}{R} = 1.45 + \frac{0.45}{1 - 0.803}$$

$$+ (0.25)(0.202)\left[17.11 + \frac{(25.2)(1 - 0.803)^{1/3}}{0.803} + \frac{1.742}{1 - 0.803}\right]$$

$$= 5.97$$

Equation (5-7.3) gives

$$\frac{C_{pL} - C_{\sigma L}}{R} = \exp(20.1T_r - 17.9)$$

$$= 0.172$$

$$C_{\sigma L} = 8.314(5.97 - 0.172) + 91$$

$$= 139.2 \text{ J/(mol·K)}$$

The experimental value is 152.7 J/(mol·K) [71], so error = $(139.2 - 152.7)/152.7 \times 100 = -8.8\%$.

Discussion

Three methods for estimating liquid heat capacities have been described. The Chueh-Swanson method is a group contribution method and is applicable only at 20°C. The Missenard method also is a group contribution method; values for the groups are given in Table 5-11 for temperatures between 248 and 373 K. The Missenard method should not be used when $T_r > 0.75$. The Rowlinson-Bondi method, Eq. (5-7.2), is a corresponding states method and is applicable at low values of T_r as well as at values approaching unity. The Rowlinson-Bondi method requires C_p°, T_c, and ω. A comparison with experimental values is given in Table 5-12. Errors are generally less than 5 percent except for alcohols at low temperatures, for which Eq. (5-7.2) is not applicable. Other methods for estimating liquid heat capacities have been published [1, 30, 31, 49, 50, 81, 92]. These methods usually require additional parameters which result in only marginal improvement or are applicable to limited classes of compounds.

For liquid mixtures, Teja [82] has examined the extension of the multiple reference fluid method [see Eq. (3-7.5)] to liquid heat capacity prediction. This method avoids the assumption that the mixture molar heat capacity is a mole fraction average of the pure component values [15], an assumption which neglects any contribution due to the effect of temperature on heats of mixing.

TABLE 5-12 Percent Error in Liquid Heat Capacity Calculated by Eq. (5-7.2)†

Compound	T, K	$C_{\sigma L}$(exp.), J/(mol·K)	Ref.	Percent error‡
Methane	102.3	54.8	90	0
	140.5	59.8		0.8
	180.9	92.9		0.7
Propane	100	84.9	43	7.4
	150	87.9		2.3
	200	93.3		0.9
	305.5	115.1	67	4.6
	344.7	150.2		−1.1
n-Pentane	200	144.3	52	−3.1
	250	153.6		1.5
	300	167.8		0.8
	363	193.3	4	−0.2
	443	273.2		−8.3
n-Heptane	300	225.5	16,52	−0.9
	400	270.3	16	−0.1
	503	355.6	4	−4.8
n-Decane	250	297.5	52	−0.9
	320	325.5		1.2
Cyclohexane	305.3	156.6	5	−1.3
	360.9	179.9		−0.9
cis-2-Butene	305.3	131.4	71	−5.1
	349.8	152.7		−8.9
Isopropylbenzene	305.3	212.1	71	2.3
	333.1	225.5		1.6
	366.4	243.1		0.1
Ethyl alcohol	208	91.2	41	84
	294	110.0		44
	383	159.0	19	4
Acetone	297	124.7	42	3.9
Ethylene oxide	170	82.4	23	5.0
	230	82.4		2.7
	280	86.6		2.5
Ethyl ether	290	170.7	59	−5.3
Ethyl chloride	150	96.2	27	−1.6
	200	95.8		−2.1
	250	98.7		−1.2
	290	103.3		−0.2
Ethyl mercaptan	208	111.7	51	−7.5
	275	115.5		−3.2
	315	120.1		−2.2
Chlorine	200	66.5	24	−5.7
	240	65.7		−3.0

†When C_{pL} or $C_{\text{sat}L}$ was reported, it was converted to $C_{\sigma L}$.
‡Percent error = [(calc. − exp.)/exp.] × 100. Ideal-gas heat capacities were taken from Refs. 3, 18, 28, 35, 60, 76, Appendix A, and the ASPEN data bank.

Recommendations

Use the Rowlinson-Bondi method Eq. (5-7.2) to estimate the liquid heat capacity of nonpolar or slightly polar compounds. For compounds for which the critical temperature is unknown, or for alcohols at low temperatures ($T_r < 0.75$), use the Missenard group contribution method.

5-8   Vapor Phase Fugacity of a Component in a Mixture

From thermodynamics, the chemical potential or fugacity can be related to the Gibbs or Helmholtz energies. Using the latter gives

$$\mu_i \equiv \left(\frac{\partial A}{\partial N_i}\right)_{T, \underline{V}, N_{j[i]}} \tag{5-8.1}$$

The subscripts on the partial derivative indicate that the temperature, total system volume, and all mole numbers (except i) are to be held constant. Thus, one may take the Helmholtz energy function for a particular equation of state, as shown in Table 5-1, and find μ_i by differentiation. Since the functions so given are expressed as the difference in specific Helmholtz energy between the real state and the chosen reference state, one must multiply the entire expression by N, the total moles, before differentiating. Then, choosing the reference state so that $V = V°$,

$$\mu_i - \mu_i° = \frac{\partial}{\partial N_i}(\underline{A} - \underline{A}°)_{T,\underline{V},N_{j[i]}} \tag{5-8.2}$$

But this difference in chemical potential is related to fugacity by

$$\mu_i - \mu_i° = RT \ln \frac{\hat{f}_i}{\hat{f}_i°} \tag{5-8.3}$$

The fugacity $\hat{f}_i$ refers to the value for component i in the mixture and $\hat{f}_i°$ to the reference state of an ideal gas at the same temperature and composition and, in this instance, to the stipulation that $V° = V$ (or $\underline{V}° = \underline{V}$). Since

$$\hat{f}_i° = P°y_i = \frac{RTy_i}{\underline{V}°} = \frac{RTy_i}{\left(\dfrac{ZRT}{P}\right)} = \frac{Py_i}{Z} \tag{5-8.4}$$

Then

$$RT \ln \left[\frac{\hat{f}_i}{\left(\dfrac{Py_i}{Z}\right)}\right] = \frac{\partial}{\partial N_i}(\underline{A} - \underline{A}°)_{T,\underline{V},N_{j[i]}} \tag{5-8.5}$$

But from Eq. (5-3.5), with $V° = V$ multiplying by N yields

$$\underline{A} - \underline{A}° = -\int_{\infty}^{\underline{V}} \left[P - \frac{NRT}{\underline{V}}\right] d\underline{V} \tag{5-8.6}$$

With Eqs. (5-8.5), (5-8.6), and $\phi_i = \dfrac{\hat{f}_i}{Py_i}$

$$RT \ln \phi_i = -\int_\infty^{\underline{V}} \left[\left(\frac{\partial P}{\partial N_i} \right)_{T,\underline{V},N_{j[i]}} - \frac{RT}{\underline{V}} \right] d\underline{V} - RT \ln Z \tag{5-8.7}$$

or $\qquad RT \ln \phi_i = \left(\dfrac{\partial(\underline{A} - \underline{A}^\circ)}{\partial N_i} \right)_{T,\underline{V},N_{j[i]}} - RT \ln Z \tag{5-8.8}$

ϕ_i is the fugacity coefficient of i in the gas mixture.

To obtain a usable relation for ϕ_i, Eq. (5-8.7) must be integrated; but before it can be, the derivative of P with respect to N_i must be found. Thus any pressure-explicit equation of state is convenient provided that the composition dependence of all the parameters can be expressed in analytical form.

For the analytical equations of state covered in Chap. 3, mixture combining rules are given in Chap. 4; thus evaluation of the integral in Eq. (5-8.7) is possible. For example, the original Redlich-Kwong equation is given as Eq. (3-6.1), and this same relation expressed in terms of total volume would be

$$P = \frac{NRT}{\underline{V} - Nb} - \frac{aN^2}{\underline{V}(\underline{V} + Nb)} \tag{5-8.9}$$

In the differentiation indicated in Eq. (5-8.7), the variables are N, a, and b, where the parameters a and b are shown as functions of composition in Eqs. (4-5.1), (4-5.2), and (3-6.1). The final result is

$$\ln \phi_i = \ln \frac{V}{V - b} + \frac{b_i}{V - b} - \ln Z$$
$$+ \frac{ab_i}{RTb^2} \left(\ln \frac{V + b}{V} - \frac{b}{V + b} \right) - \frac{2 \sum_j y_j a_{ij}}{RTb} \ln \frac{V + b}{V} \tag{5-8.10}$$

For all the analytical equations of state, the working equations for $\ln \phi_i$ are given in Table 5-13.

It is difficult to evaluate these expressions, since fugacity coefficients themselves are difficult to determine. Presumably, if the mixture equation of state is a valid representation, the derived property ϕ_i should also be accurate. This assumes, of course, that the equation of state not only yields accurate predictions of volumetric properties but also that it yields accurate derivatives of pressure with respect to mole numbers. These two attributes are not necessarily compatible.

Vapor phase fugacity expressions are of value in vapor-liquid equilibrium calculations, as described in Chap. 8.

TABLE 5-13 Fugacity Coefficient Expressions

$$\phi_i \equiv \frac{\hat{f}_i}{y_i P}$$

Virial, $Z = 1 + \dfrac{BP}{RT}$ [Eqs. (3-5.2a) and (4.4.1)]

$$\ln \phi_i = \left(2 \sum_j y_j B_{ij} - B \right) \frac{P}{RT} \qquad (5\text{-}8.11)$$

Cubic, $P = \dfrac{RT}{V-b} - \dfrac{a}{V^2 + ubV + wb^2}$ [Eqs. (3-6.1), (4-5.1), and (4-5.2) and Table 3-5]

$$\ln \phi_i = \frac{b_i}{b}(Z-1) - \ln(Z - B^*) + \frac{A^*}{B^*\sqrt{u^2 - 4w}} \left(\frac{b_i}{b} - \delta_i \right) \ln \frac{2Z + B^*(u + \sqrt{u^2 - 4w})}{2Z + B^*(u - \sqrt{u^2 - 4w})} \qquad (5\text{-}8.12)$$

where
$$\frac{b_i}{b} = \frac{T_{ci}/P_{ci}}{\sum_j y_j T_{cj}/P_{cj}} \qquad (5\text{-}8.13)$$

$$\delta_i = \frac{2a_i^{1/2}}{a} \sum_j x_j a_j^{1/2} (1 - \bar{k}_{ij}) \qquad (5\text{-}8.14)$$

If all $\bar{k}_{ij} = 0$, this reduces to
$$\delta_i = 2\left(\frac{a_i}{a} \right)^{1/2} \qquad (5\text{-}8.15)$$

Lee-Kesler [Eqs. (3-7.1) to (3-7.4) and Table 4-3]

$$\ln \phi_i = \ln \left(\frac{f}{P} \right)_m + \frac{H^\circ - H}{TRT_{cm}} \left[\sum_{j \ne i} y_j \left(\frac{dT_{cm}}{dy_j} \right)_{y_k} \right] + \frac{Z_m - 1}{P_{cm}} \left[\sum_{j \ne i} y_j \left(\frac{dP_{cm}}{dy_j} \right)_{y_k} \right] - \ln \left(\frac{f}{P} \right)_m^{(1)} \sum_{j \ne i} y_j \left(\frac{d\omega_m}{dy_j} \right)_{y_k} \qquad (5\text{-}8.16)$$

$$\left(\frac{dT_{cm}}{dy_j} \right)_{y_k} = \left[2 \sum_l y_l (V_{cij}^{1/4} T_{cij} - V_{cli}^{1/4} T_{cli}) - \frac{0.25}{V_{cm}^{3/4}} \left(\frac{dV_{cm}}{dy_j} \right)_{y_k} T_{cm} \right] \Big/ V_{cm}^{1/4} \qquad (5\text{-}8.17)$$

$$\left(\frac{dV_{cm}}{dy_j} \right)_{y_k} = 2 \sum_l y_l (V_{cij} - V_{cli}) \qquad (5\text{-}8.18)$$

$$\left(\frac{dP_{cm}}{dy_j} \right)_{y_k} = P_{cm} \left[-\frac{0.085(\omega_j - \omega_i)}{Z_{cm}} + \frac{1}{T_{cm}} \left(\frac{dT_{cm}}{dy_j} \right)_{y_k} - \frac{1}{V_{cm}} \left(\frac{dV_{cm}}{dy_j} \right)_{y_k} \right] \qquad (5\text{-}8.19)$$

Note: In Eqs. (5-8.16) to (5-8.19), $k \ne i, j$. $\ln (f/P)_m$ is given in Eq. (5-4.11); $(H^\circ - H)/RT_{cm}$ is given by Eq. (5-4.3); and T_{cm}, V_{cm}, ω_m, and P_{cm} are given in Table 4-3. log $(f/P)_m^{(1)}$ [not $\ln (f/P)_m^{(1)}$] is given in Table 5-7.

Notation

a	cubic-equation-of-state constant, Table 3-5
A	Helmholtz energy, J/mol
$\underline{A}$	Helmholtz energy, J
b	cubic-equation-of-state constant, Table 3-5
C	heat capacity, J/(mol·K); C_p, at constant pressure; C_v, at constant volume; $C_{\sigma L}$, variation of saturated liquid enthalpy with temperature; $C_{\text{sat}L}$, $(dQ/dT)_{SL}$
f	fugacity, bar; $\hat{f_i}$ fugacity of i in a mixture
G	Gibbs energy, J/mol
H	enthalpy, J/mol
ΔH_v	enthalpy of vaporization, J/mol
M	molecular weight
N	total moles
P	pressure, usually bar; P_c, at the critical point; P_r, P/P_c
Q	heat, J
R	gas constant, 8.314 J/(mol·K)
S	entropy, J/(mol·K)
T	temperature, K; T_c, at the critical point; T_r, T/T_c; T_b, at the normal boiling point
U	internal energy, J/mol
V	volume, cm³/mol; V_c, at the critical point; V_r, V/V_c
$\underline{V}$	volume, cm³
x_i	mole fraction i
y_i	mole fraction i
Z	compressibility factor; Z_c, at the critical point

GREEK

δ_T, δ_v	parameters in Eqs. (5-6.7) and 5-6.11)
θ	surface fraction, Eqs. (5-6.3) and (5-6.15)
μ	chemical potential
ν_{ij}	interaction parameter in Eq. (5-6.8)
τ_{ij}	interaction parameter in Eq. (5-6.4)
ϕ_i	fugacity coefficient, $\hat{f_i}/Py_i$
ϕ	volume fraction defined in Eq. (5-6.1)
ψ_T, ψ_v	parameter in Eqs. (5-6.6) and (5-6.10)
ω	Pitzer acentric factor

SUPERSCRIPTS

°	reference state or an ideal-gas state
(0)	simple fluid function
(R)	simple fluid function for the reference fluid
R	reference fluid
SL	saturated liquid
SV	saturated vapor
L	liquid
EX	excess function
(1)	deviation function

SUBSCRIPTS

b	normal boiling point
c	critical state
SCL	subcooled liquid
SL	saturated liquid
SV	saturated vapor
m	mixture
T	true critical property of mixture
σ_L	saturated liquid state

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Chapter

6

Thermodynamic Properties of Ideal Gases

6-1 Scope and Definitions

Methods are described to estimate the enthalpy and Gibbs energy of formation as well as the entropy for organic compounds in the ideal-gas state. The reference temperature is 298.15 K, and the reference pressure is *one atmosphere*. In addition, ideal-gas heat capacity estimation techniques are presented to allow one to determine C_p° as a function of temperature.

The enthalpy of formation is defined as the isothermal enthalpy change in a synthesis reaction from the elements in their standard states. In such a reaction scheme, the elements are assumed initially to be at reaction temperature, at 1 atm, and in their most stable phase, e.g., diatomic oxygen as an ideal gas, carbon as a solid in the form of β-graphite, etc. Ordinarily one need not be concerned with the numerical values of the enthalpy of formation of the constituent elements, since, to obtain a standard enthalpy of *reaction,* the enthalpies of formation of all elements cancel. For a general reaction

$$aA + bB = cC + dD$$

the standard enthalpy change to form products C and D from A and B in stoichiometric amounts when reactants and products are pure, at T and 1 atm, is given by

$$\Delta H^\circ = c\,\Delta H_f^\circ\,(C) + d\,\Delta H_f^\circ\,(D) - a\,\Delta H_f^\circ\,(A) - b\,\Delta H_f^\circ\,(B) \qquad (6\text{-}1.1)$$

At 298 K, if A, B, C, and D are elements in their most stable phase configuration, the value of ΔH_f° is set equal to zero.

Reported enthalpies of formation are normally available only at 298 K. At other temperatures,

$$\Delta H_f^\circ (T) = \Delta H_f^\circ (298 \text{ K}) + \int_{298}^{T} \Delta C_p^\circ \, dT \tag{6-1.2}$$

where

$$\Delta C_p^\circ = \sum_j \nu_j C_{pj}^\circ \tag{6-1.3}$$

that is, ΔC_p° is the sum of the heat capacities of the compound and the constituent elements, each element in its standard state, and each multiplied by the appropriate stoichiometric multiplier ν_j. For most elements, there is no difficulty in obtaining C_p°. As examples, oxygen at 298 K has a standard state as an ideal gas and $C_p^\circ (O_2)$ is then the heat capacity of diatomic oxygen as an ideal gas. Or, for carbon, one would need the heat capacity C_p° (β-graphite) as a function of temperature. However, in some instances, care is necessary to include phase change enthalpies in addition to heat capacities when calculating ΔH_f° as a function of temperature. A case in point would be for compounds containing bromine. The standard state for diatomic bromine at 298 K is the pure liquid at its vapor pressure. For this state, ΔH_f° (Br_2) $= 0$. Then, in Eq. (6-1.2), to determine $\Delta H_f^\circ (T)$ for a compound containing bromine, one must integrate the heat capacity of the liquid bromine up to its normal boiling point at 1 atm, add the enthalpy of vaporization at T_b, and, if $T > T_b$, add the integral of the ideal-gas heat capacity between T_b and T.

Another way to write Eq. (6-1.1) is to combine Eq. (6-1.2) and Eq. (6-1.3):

$$\Delta H^\circ (T) = \sum_j \nu_j \Delta H_{fj}^\circ (298 \text{ K}) + \sum_j \int_{298}^{T} \nu_j C_{pj}^\circ \, dT \tag{6-1.4}$$

where ν_j is the stoichiometric multiplier in the synthesis reaction (negative for reactants and positive for products). Thus, to determine enthalpies of reaction, one needs to know the enthalpy of formation at 298 K as well as the ideal-gas (or element) heat capacities of all reactants and products.

The Gibbs energy of formation ΔG_f° is defined in a manner analogous to that for ΔH_f°, and the standard Gibbs energy of reaction $\Delta G^\circ (T)$ is written in a form similar to that of Eq. (6-1.1). Unless otherwise stated, all reactants and products are pure, ideal gases at temperature T and 1 atm. (As noted earlier, elements which are not normally gases at T are defined somewhat differently [10, 24].)

Finally, the standard entropies of most elements and all compounds, $S^\circ (T)$, apply to materials in an ideal-gas state at 1 atm and at a temperature T. This entropy is often termed an *absolute* entropy because it is

relative to a value of zero at absolute zero temperature in a perfectly ordered solid state. The entropy of formation could also have been introduced, but no estimation scheme yields this property directly. For use in chemical reactions, since the standard-state entropies of the elements cancel, one may employ $S°$ (T) directly; i.e., for the general reaction introduced above,

$$\Delta S° \ (T) = cS_c° \ (T) + dS_d° \ (T) - aS_a° \ (T) - bS_b° \ (T) \tag{6-1.5}$$

$\Delta S° \ (T)$ may be expressed in terms of $S°$ (298 K) for reactants and products in a manner similar to Eq. (6-1.4),

$$\Delta S° \ (T) = \sum_j \nu_j S_j° \ (298 \ \text{K}) + \sum_j \int_{298}^{T} \nu_j C_p° \ d \ln T \tag{6-1.6}$$

The Gibbs energy change for a chemical reaction $\Delta G° \ (T)$ may be written as

$$\Delta G° \ (T) = \Delta H° \ (T) - T \ \Delta S° \ (T) \tag{6-1.7}$$

where $\Delta H° \ (T)$ and $\Delta S° \ (T)$ are found from Eqs. (6-1.4) and (6-1.6). The Gibbs energy change is related to the chemical equilibrium constant by

$$\ln K = \frac{-\Delta G°}{RT} \tag{6-1.8}$$

Because of the exponential character of this equation, small errors in estimating $\Delta G° \ (T)$ are amplified when calculating K. We illustrate this in Fig. 6-1. Here we define Y = true value of $\Delta G° \ (T)/RT$ and show how the equilibrium constant is affected when we overestimate (or underestimate) $\Delta G° \ (T)/RT$. For example, if the true value of $\Delta G° \ (T)/RT$ were 6 and we overestimated by 15 percent, then $\ln K_{est} = -(6)(1.15)$, and $K_{est} = 10^{-3}$, whereas K_{true} is 2.5×10^{-3}. Note that estimation errors are more serious when $|Y| \gg 0$ because the slope on the plot is proportional to Y.

6-2   Estimation Methods

Since the properties of compounds treated in this chapter refer to those of an *ideal gas*, intermolecular forces play no role in their estimation. Also, by the same reasoning, the law of corresponding states, used so widely in other chapters, is inapplicable. All estimation methods for $C_p°$, $\Delta H_f°$, $\Delta G_f°$, and $S°$ involve some group estimation scheme related to the molecular structure. Benson [3] and Benson and Buss [4] have pointed out a hierarchy of such methods. The most simple methods would be those which assign contributions based on the *atoms* present in the
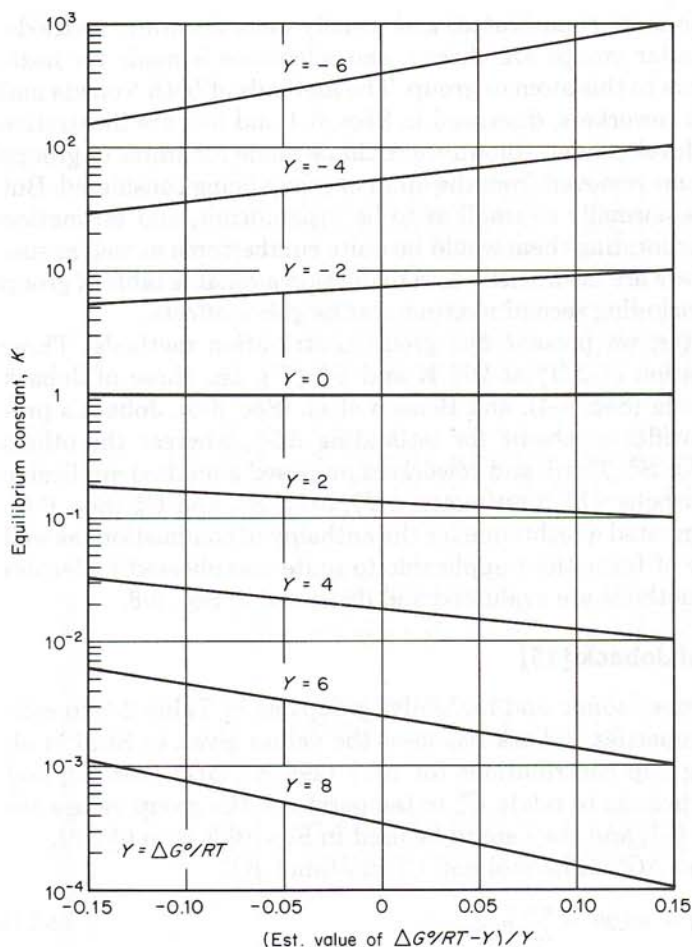
Figure 6-1 Effect of errors in $\Delta G°/RT$ on the equilibrium constant.

molecule. Although exact for molecular weights and even reasonable for a few other properties, e.g., the liquid molar volume at the normal boiling point, such methods are completely inadequate for the properties discussed in this chapter.

Only slightly more complicated are methods which assign contributions to various chemical bonds. Such techniques are easy to use but again do not normally yield very accurate results. A more successful method assigns contributions to common molecular groupings, for example, $-CH_3$, $-NH_2-$, $-COOH$, and, by simple additivity, one can then estimate ideal-gas properties from a table of group values. The Joback method discussed in Sec. 6-3 employs this approach.

Proceeding to more complicated, and usually more accurate, methods, atoms or molecular groups are chosen, and allowance is made for next-nearest neighbors to this atom or group. The methods of both Yoneda and Benson and his coworkers, discussed in Secs. 6-4 and 6-6, are illustrative of this type of development. Allowance could be made for atoms or groups two or more atoms removed from the atom or group being considered. But such effects are normally so small as to be insignificant, and estimation techniques incorporating them would be quite cumbersome as well as suspect because there are insufficient data to develop a reliable table of group contributions including second next-nearest neighbor effects.

In this chapter, we present five group contribution methods. Three allow an estimation of ΔH_f° at 298 K and C_p° (T), i.e., those of Joback (Sec. 6-3), Yoneda (Sec. 6-4), and Benson et al. (Sec. 6-6). Joback's procedure also provides a scheme for estimating ΔG_f°, whereas the others yield methods for S°. Thinh and coworkers proposed a method applicable only to hydrocarbons which estimates ΔH_f°, ΔG_f°, S°, and C_p° (Sec. 6-5). Cardozo has suggested a technique for the enthalpy of combustion (as well as the enthalpy of formation) applicable to quite complicated molecules (Sec. 6-7). All methods are evaluated and discussed in Sec. 6-8.

6-3 Method of Joback [15]

Choosing the same atomic and molecular groups as in Table 2-2 to estimate critical properties, Joback has used the values given in Stull et al. [25] to obtain group contributions for ΔH_f° (298 K), ΔG_f° (298 K), and polynomial coefficients to relate C_p° to temperature. His group values are shown in Table 6-1, and they are to be used in Eqs. (6-3.1) to (6-3.3).

With ΔH_f° and ΔG_f° in kJ/mol and C_p° in J/(mol·K),

$$\Delta H_f^\circ \ (298 \text{ K}) = 68.29 + \sum_j n_j \, \Delta_H \tag{6-3.1}$$

$$\Delta G_f^\circ \ (298 \text{ K}) = 53.88 + \sum_j n_j \, \Delta_G \tag{6-3.2}$$

$$C_p^\circ = \left(\sum_j n_j \, \Delta_a - 37.93 \right) + \left(\sum_j n_j \, \Delta_b + 0.210 \right) T$$
$$+ \left(\sum_j n_j \, \Delta_c - 3.91 \times 10^{-4} \right) T^2 + \left(\sum_j n_j \, \Delta_d \right)$$
$$+ 2.06 \times 10^{-7} \right) T^3 \tag{6-3.3}$$

where n_j is the number of groups of the jth type and the Δ contributions are for the jth atomic or molecular group. The temperature T is in kelvins.

Example 6-1 Estimate ΔH_f° (298 K), ΔG_f° (298 K), and the isobaric ideal-gas heat capacity of butyronitrile at 500 K by using Joback's additive-group method.

TABLE 6-1 Joback Group Contributions for Ideal-Gas Properties

	Δ_H	Δ_G	Δ_a	Δ_b	Δ_c	Δ_d
	kJ/mol	kJ/mol	\.\.\.\.\.\.\.\.\.\.	\.\.\.\.\.\.\. J/mol K	\.\.\.\.\.\.\.\.	\.\.\.\.\.\.\.
Non-ring increments						
—CH₃	-76.45	-43.96	1.95E+1	-8.08E-3	1.53E-4	-9.67E-8
>CH₂	-20.64	8.42	-9.09E-1	9.50E-2	-5.44E-5	1.19E-8
>CH—	29.89	58.36	-2.30E+1	2.04E-1	-2.65E-4	1.20E-7
>C<	82.23	116.02	-6.62E+1	4.27E-1	-6.41E-4	3.01E-7
=CH₂	-9.63	3.77	2.36E+1	-3.81E-2	1.72E-4	-1.03E-7
=CH—	37.97	48.53	-8.00	1.05E-1	-9.63E-5	3.56E-8
=C<	83.99	92.36	-2.81E+1	2.08E-1	-3.06E-4	1.46E-7
=C=	142.14	136.70	2.74E+1	-5.57E-2	1.01E-4	-5.02E-8
≡CH	79.30	77.71	2.45E+1	-2.71E-2	1.11E-4	-6.78E-8
≡C—	115.51	109.82	7.87	2.01E-2	-8.33E-6	1.39E-9
Ring increments						
—CH₂—	-26.80	-3.68	-6.03	8.54E-2	-8.00E-6	-1.80E-8
>CH—	8.67	40.99	-2.05E+1	1.62E-1	-1.60E-4	6.24E-8
>C<	79.72	87.88	-9.09E+1	5.57E-1	-9.00E-4	4.69E-7
=CH—	2.09	11.30	-2.14	5.74E-2	-1.64E-6	-1.59E-8
=C<	46.43	54.05	-8.25	1.01E-1	-1.42E-4	6.78E-8
Halogen increments						
—F	-251.92	-247.19	2.65E+1	-9.13E-2	1.91E-4	-1.03E-7
—Cl	-71.55	-64.31	3.33E+1	-9.63E-2	1.87E-4	-9.96E-8
—Br	-29.48	-38.06	2.86E+1	-6.49E-2	1.36E-4	-7.45E-8
—I	21.06	5.74	3.21E+1	-6.41E-2	1.26E-4	-6.87E-8

TABLE 6-1 Joback Group Contributions for Ideal-Gas Properties
(Continued)

	Δ_H	Δ_G	Δ Values				
	kJ/mol	kJ/mol	Δ_a	Δ_b	Δ_c	Δ_d	
			•••••••••••••••••••••••• J/mol K ••••••••••••••••••••••••				
Oxygen increments							
-OH (alcohol)	-208.04	-189.20	2.57E+1	-6.91E-2	1.77E-4	-9.88E-8	
-OH (phenol)	-221.65	-197.37	-2.81	1.11E-1	-1.16E-4	4.94E-8	
-O- (nonring)	-132.22	-105.00	2.55E+1	-6.32E-2	1.11E-4	-5.48E-8	
-O- (ring)	-138.16	-98.22	1.22E+1	-1.26E-2	6.03E-5	-3.86E-8	
>C=0 (nonring)	-133.22	-120.50	6.45	6.70E-2	-3.57E-5	2.86E-9	
>C=0 (ring)	-164.50	-126.27	3.04E+1	-8.29E-2	2.36E-4	-1.31E-7	
0=CH- (aldehyde)	-162.03	-143.48	3.09E+1	-3.36E-2	1.60E-4	-9.88E-8	
-COOH (acid)	-426.72	-387.87	2.41E+1	4.27E-2	8.04E-5	-6.87E-8	
-COO- (ester)	-337.92	-301.95	2.45E+1	4.02E-2	4.02E-5	-4.52E-8	
=0 (except as above)	-247.61	-250.83	6.82	1.96E-2	1.27E-5	-1.78E-8	
Nitrogen Increments							
-NH$_2$	-22.02	14.07	2.69E+1	-4.12E-2	1.64E-4	-9.76E-8	
>NH (nonring)	53.47	89.39	-1.21	7.62E-2	-4.86E-5	1.05E-8	
>NH (ring)	31.65	75.61	1.18E+1	-2.30E-2	1.07E-4	-6.28E-8	
>N- (nonring)	123.34	163.16	-3.11E+1	2.27E-1	-3.20E-4	1.46E-7	
-N= (nonring)	23.61	-	-	-	-	-	
-N= (ring)	55.52	79.93	8.83	-3.84E-3	4.35E-5	-2.60E-8	
=NH	93.70	119.66	5.69	-4.12E-3	1.28E-4	-8.88E-8	
-CN	88.43	89.22	3.65E+1	-7.33E-2	1.84E-4	-1.03E-7	
-NO$_2$	-66.57	-16.83	2.59E+1	-3.74E-3	1.29E-4	-8.88E-8	
Sulfur increments							
-SH	-17.33	-22.99	3.53E+1	-7.58E-2	1.85E-4	-1.03E-7	
-S- (nonring)	41.87	33.12	1.96E+1	-5.61E-3	4.02E-5	-2.76E-8	
-S- (ring)	39.10	27.76	1.67E+1	4.81E-3	2.77E-5	-2.11E-8	

solution Butyronitrile contains one $-CH_3$, two $-CH_2-$, and one $-CN$. From Table 6-1

Group	n_j	$n_j \Delta_H$	$n_j \Delta_G$
$-CH_3$	1	-76.45	-43.96
$-CH_2-$	2	-41.28	16.84
$-CN$	1	88.43	89.22
		$\Sigma n_j \Delta_H = -29.30$	$\Sigma n_j \Delta_G = 62.10$

With Eqs. (6-3.1) and (6-3.2)

$$\Delta H_f^\circ \ (298 \ K) = 68.29 - 29.30 = 38.99 \ \text{kJ/mol}$$

$$\Delta G_f^\circ \ (298 \ K) = 53.88 + 62.10 = 115.98 \ \text{kJ/mol}$$

The literature values for these two properties are 34.08 and 108.73 kJ/mol, respectively [25], thus the differences, estimated $-$ literature, are

$\Delta H_f^\circ \ (298 \ K)$ Difference $= 38.99 - 34.08 = 4.91$ kJ/mol

$\Delta G_f^\circ \ (298 \ K)$ Difference $= 115.98 - 108.73 = 7.25$ kJ/mol

For the heat capacity,

Group	n_j	$n_j \Delta_a$	$n_j \Delta_b$	$n_j \Delta_c$	$n_j \Delta_d$
$-CH_3$	1	$1.95 \ E+1$	$-8.08 \ E-3$	$1.53 \ E-4$	$-9.67 \ E-8$
$-CH_2-$	2	-1.82	$1.90 \ E-1$	$-1.09 \ E-4$	$2.38 \ E-8$
$-CN$	1	$3.65 \ E+1$	$7.33 \ E-2$	$1.84 \ E-4$	$-1.03 \ E-7$
		54.18	0.109	$2.28 \ E-4$	$-1.76 \ E-7$

Then, with Eq. (6-3.3),

$$C_p^\circ \ (500 \ K) = (54.18 - 37.93) + (0.109 + 0.210) \ (500) + (2.28 \ E-4$$
$$- 3.91 \ E-4) \ (500)^2 + (-1.76 \ E-7 + 2.06 \ E-7) \ (500)^3$$
$$= 138.75 \ \text{J/(mol·K)}$$

The literature value is 138.37 J/(mol·K), so the error is

$$\text{Error} = \frac{138.75 - 138.37}{138.37} \times 100 = 0.3\%$$

Comparisons between estimated and literature values of ΔH_f° (298 K) are shown in Table 6-7, for ΔG_f° (298 K) in Table 6-9, and for C_p° (T) in Table 6-6. A comparison of this technique with others is presented in Sec. 6-8.

6-4 Method of Yoneda [29]

Yoneda modified a group contribution technique for ideal-gas properties that was originally proposed by Anderson et al. [2, 14]. In this method,

one begins with a *base* molecule and sequentially modifies the structure by substituting other groups to arrive at the final structure. Each substitution has a group contribution value, and the values are summed to arrive at the final value of the property. The mechanics of the method are described in detail below. With it one can estimate ΔH_f° (298 K), S° (298 K), and the polynomial constants for C_p°. Equations (6-4.1) to (6-4.3) are used.

$$\Delta H_f^\circ \ (298 \ \text{K}) = \sum_j n_j \, \Delta_H \tag{6-4.1}$$

$$S^\circ \ (298 \ \text{K}) = \sum_j n_j \, \Delta_S \tag{6-4.2}$$

$$C_p^\circ \ (T) = \sum_j n_j \, \Delta_a + \left(\sum_j n_j \, \Delta_b \right) \left(\frac{T}{1000} \right) + \left(\sum_j n_j \, \Delta_c \right) \left(\frac{T}{1000} \right)^2 \tag{6-4.3}$$

Δ is the contribution (Table 6-2), and n_j is the number of times the contribution is required. ΔH_f° (298 K) is estimated in kJ/mol, and both C_p° (T) and S° (298 K) are estimated in J/(mol·K). The temperature is in kelvins.

To use this method, one must first select a *base* group from which to synthesize the desired molecule. The base groups allowed are:

Methane
Cyclopentane
Cyclohexane
Benzene
Naphthalene

Compounds which cannot be synthesized from these groups, e.g., thiophene, cannot be treated. There are contributions for each base group (Table 6-2a), and for subsequent substitutions (Tables 6-2b to 6-2e). Corrections are also necessary in some cases (Table 6-2f).

To introduce the method, let us initially limit the discussion to hydrocarbons. Later we will demonstrate how functional groups containing atoms other than carbon and hydrogen are inserted.

We begin with the appropriate base group and proceed in a series of steps:

1. The desired structure is built up by substituting $-CH_3$ groups for hydrogen atoms. The *first* substitution on the base group is termed a *primary methyl substitution*. For methane, only a single type of primary substitution is possible and, of course, ethane is formed. For ring compounds as base groups, one may have several types of primary methyl substitutions for hydrogens on the ring. For example, if the final compound were to consist of a 1,3-*trans* form of cyclohexane, we would require a *first* primary methyl substitution as well as a *second* primary methyl substitution of the 1,3-*trans* type. (At this stage, our compound would be 1,3-

TABLE 6-2   Yoneda Group Contributions for Ideal-Gas Properties[a]

Table 6-2a   Contributions for Base Groups

Base Group	ΔH	ΔS	Δa	Δb	Δc
Methane	-74.90	186.31	16.71	65.65	-9.96
Cyclopentane	-77.29	293.08	-41.95	474.03	-182.71
Cyclohexane	-123.22	298.44	-52.25	600.18	-231.07
Benzene	82.98	269.38	-22.52	402.81	-171.53
Naphthalene	151.06	335.87	-28.43	623.67	-269.09

Table 6-2b   Contributions for Primary Methyl Substitutions

Base Group	ΔH	ΔS	Δa	Δb	Δc
Methane	-9.84	43.33	-9.92	103.87	-43.54
Cyclopentane					
First primary	-34.46	49.28	8.75	68.29	-23.19
Second primary					
to form:					
1,1	-26.63	17.17	-6.03	116.43	-55.60
1,2 (cis)	-17.88	24.03	-3.64	110.53	-53.26
1,2 (trans)	-25.04	24.70	-2.47	107.64	-52.17
1,3 (cis)	-24.20	24.70	-2.47	107.64	-52.17
1,3 (trans)	-21.94	24.70	-2.47	107.64	-52.17
Cyclohexane					
First primary	-33.66	46.35	11.60	81.27	-39.61
Second primary					
to form:					
1,1	-24.24	20.47	13.52	111.49	-41.03
1,2(cis)	-15.41	29.98	-8.00	100.06	-38.73
1,2(trans)	-23.24	26.38	-5.82	103.37	-43.25
1,3(cis)	-28.01	25.92	-6.32	95.21	-33.03
1,3(trans)	-19.80	31.69	-4.31	88.49	-32.20
1,4(cis)	-19.89	25.92	-4.31	88.47	-32.30
1,4(trans)	-27.84	20.26	-8.42	107.68	-44.05
Benzene					
First primary	-35.50	47.94	5.78	64.68	-19.51
Second primary					
to form:					
1,2	-27.80	36.43	12.48	50.03	-11.97
1,3	-29.14	41.66	5.02	64.81	-19.64
1,4	-28.72	36.22	5.48	60.33	-16.16
1,2,3	-30.40	42.87	14.15	29.27	9.67
1,2,4	-33.49	43.63	16.41	18.63	16.24
1,3,5	-34.22	26.84	6.20	58.41	-14.74

trans-dimethylcyclohexane.) The various primary methyl substitution group values are shown in Table 6-2b. These substitutions must be made before any secondary methyl substitutions.

2. After making the primary methyl substitutions, we continue to replace hydrogen atoms in the synthesis procedure with additional $-CH_3$ groups. Each of these steps is termed a *secondary methyl substitution*. Contributions for such substitutions depend on the type of carbon upon which the substitution is made as well as upon the type of adjacent carbon

TABLE 6-2   Yoneda Group Contributions for Ideal-Gas Properties[a]
(*Continued*)

Table 6-2b   Contributions for Primary Methyl Substitutions (continued)

Base Group	ΔH	ΔS	Δa	Δb	Δc
Naphthalene					
First primary					
Position 1	-34.12	41.83	6.36	37.39	-32.11
Position 2	-34.88	44.42	10.68	61.80	-20.18
Second primary					
to form:					
1,2	-26.42	30.31	13.06	64.81	-24.58
1,3	-27.76	35.59	5.61	79.59	-32.24
1,4	-27.34	30.10	6.07	75.11	-28.76
2,3	-26.42	30.31	13.06	64.81	-24.58

Table 6-2c   Contributions for Secondary Methyl Substitutions

Type Number A	B	ΔH	ΔS	Δa	Δb	Δc
1	1	-21.10	43.71	-3.68	98.22	-42.29
1	2	-20.60	38.90	1.47	81.48	-31.48
1	3	-15.37	36.63	-0.96	91.69	-38.98
1	4	-15.37	36.63	-0.96	91.69	-38.98
1	9	-19.68	45.34	1.55	88.59	-37.68
2	1	-28.76	21.48	-2.09	95.75	-41.70
2	2	-26.59	27.34	-0.63	90.73	-37.56
2	3	-22.23	27.38	-4.90	97.68	-41.66
2	4	-20.68	27.51	-1.21	92.11	-38.02
2	9	-24.37	28.09	-3.18	90.43	-36.34
3	1	-31.48	11.76	-2.76	107.77	-49.28
3	2	-28.64	18.00	-6.91	111.79	-51.71
3	3	-20.77	25.96	-6.91	111.79	-51.75
3	4	-23.70	4.56	-4.19	129.62	-66.36
3	9	-26.13	28.09	-3.18	90.43	-36.34

atoms. We designate by the letter A the carbon atom where the substitution is made and by the letter B the *highest type number* (see below) of carbon adjacent to A. The type numbers are as follows:

Type				
1	2	3	4	9
$-CH_3$	$-CH_2-$	$>CH-$	$>C<$	C in aromatic ring

Contributions for secondary methyl substitutions are given in Table 6-2c. As an example, assume we were interested in 2-methylbutane. The sequential steps would be:

Table 6-2d Multiple Bond Contributions Replacing Single Bonds

Bond type	ΔH	ΔS	Δa	Δb	Δc
1=1	137.08	-10.05	0.50	-32.78	3.73
1=2	126.23	-5.99	3.81	-50.95	16.33
1=3	116.98	0.71	12.81	-71.43	27.93
2=2 (cis)	118.49	-6.32	-6.41	-37.60	11.30
2=2 (trans)	114.51	-11.39	9.17	-67.57	26.80
2=3	114.72	0.59	-1.05	-54.09	21.23
3=3	115.97	-2.09	5.90	-95.92	57.57
1≡1	311.62	-28.68	19.18	-98.81	22.99
1≡2	290.98	-20.81	16.54	-117.15	40.74
2≡2	274.40	-23.95	12.85	-127.11	51.71
Adjacent double bonds	41.41	-13.27	9.76	-7.79	2.14
Conjugated double bonds	-15.32	-17.00	-6.70	37.30	-27.51
Double bond conjugated with aromatic ring	-7.20	-9.50	5.36	-9.09	5.19
Triple bond conjugated with aromatic ring	8.79	-20.10	-3.77	4.61	0.42
Conjugated triple bonds	17.58	-20.52	3.35	14.65	-14.65
Conjugated double and triple bonds	13.82	-5.86	12.56	22.19	9.63

Table 6-2e Fundamental Contributions (Replacing CH_n Groups)

Functional group	ΔH	ΔS	Δa	Δb	Δc
=O (aldehyde)	-10.13	-54.43	17.12	-214.20	84.32
=O (ketone)	-29.68	-84.53	6.32	-148.59	36.68
-OH	-119.07	8.62	7.29	-65.73	24.45
*-OH	-146.58	-1.26	12.02	-49.82	24.28
-O-	-85.54	-5.28	13.27	-85.37	38.60
*-O-	-97.85	-15.07	18.00	-69.50	38.10
-OOH	-103.41				
-OO-	-21.86				
-COOH	-350.39	53.05	7.91	29.22	-26.67
*-COOH	-337.87	51.92	-8.04	25.20	-4.56
-COO-	-306.14	54.85	-17.58	1.26	7.95
*-COO-	-317.90	54.85	-17.58	1.26	7.95

Base group → methane

Primary methyl substitution → ethane

Secondary methyl substitutions

A=1, B=1 → propane

A=1, B=2 → n-butane

A=2, B=2 → 2-methylbutane

3. Next, we insert any necessary double or triple bonds in the molecule. Contributions for such substitutions are shown in Table 6-2d, and they

TABLE 6-2   Yoneda Group Contributions for Ideal-Gas Properties[a]
(*Continued*)

Table 6-2e   Fundamental Contributions (Replacing CH$_n$ Groups)

Functional group	Δ_H	Δ_S	Δ_a	Δ_b	Δ_c
*-OOC-	-310.33				
-COOCO-	-470.26	116.94	-5.28	124.72	-69.29
-COO$_2$CO-	-392.30				
-OOCH	-276.04	71.80	7.91	29.22	-26.67
-CO$_3$-	-490.57				
-F	-154.28	-16.62	4.23	-76.62	24.58
*-F	-165.34	-18.05	6.49	-59.54	18.38
*-F (ortho)	-143.36	-12.85	5.90	-78.92	32.45
-COF	-355.71	57.36	14.24	-18.00	4.61
*-COF	-351.69				
-Cl	2.05	-5.90	7.45	-64.90	14.95
*-Cl	9.88	-3.98	10.72	-83.40	31.07
-COCl	-159.35	53.97	22.65	-23.57	-2.43
*-COCl	-155.41				
-Br	49.57	13.10	11.14	-49.95	13.06
*-Br	57.61	7.29	12.31	-70.38	28.93
-COBr	-105.80	68.66	20.93	-43.54	9.21
*-COBr	-98.56				
-I	101.19	14.57	11.39	-72.56	18.30
*-I	115.18	8.79	12.56	-92.95	34.33
-COI	-38.06	88.34	23.45	-33.08	9.63
*-COI	-30.98				
-SH	60.37	24.07	14.40	-65.98	28.43
*-SH	64.14	19.76	12.14	-42.45	19.43
-S-	69.67	21.65	17.12	-83.65	46.05
*-S-	71.01	17.17	15.07	-60.29	38.64
-SS-	79.88	63.51	35.63	-58.45	20.43
-SO-	-43.17				
*-SO-	-39.77				
-SO$_2$-	-280.10				
-*SO$_2$-	-276.66				
-SO$_3$H	1183.61				
-OSO$_2$-	-379.78				
-OSO$_3$-	-583.56				

depend upon the type numbers of the carbon atoms involved. As an example, for 2-methyl-2-butene, we would first synthesize 2-methylbutane as above and insert a double bond of the type 2=3. Corrections are also given in Table 6-2*d* for adjacent and conjugated double and triple bonds.

With steps 1 to 3 we can synthesize hydrocarbons and estimate their ideal-gas properties.

For nonhydrocarbons, one must first prepare a suitable hydrocarbon and then insert the desired functional groups by substituting for $-CH_n-$

Table 6-2e Fundamental Contributions (Replacing CHₙ Groups) (continued)

Functional group	ΔH	ΔS	Δa	Δb	Δc
-NH₂	61.50	13.10	7.49	-37.68	13.19
*-NH₂	39.44	2.05	8.83	-14.40	4.40
-NH-	87.00	-0.21	1.38	-24.62	7.75
*-NH-	57.61	-11.30	2.51	-1.26	-0.84
-N<	110.74	-5.86	0.04	-18.59	4.40
*-N<	80.72	-16.75	1.26	4.61	-4.19
=N- (keto)	187.15				
-N=N-	266.28				
-NHNH₂	170.15	49.24			
*-NHNH₂	153.61				
-N(NH₂)-	187.86	31.53			
*-N(NH₂)-	171.24				
-NHNH-	195.86	39.10			
*-NHNH-	179.20				
-CN	172.66	6.70	14.32	-53.42	14.70
*-CN	171.49	3.94	17.79	-47.60	20.18
-NC	235.05	17.29	17.58	-47.73	20.10
=NOH	92.11				
-CONH₂	-153.74	77.46	15.07	23.86	-12.56
*-CONH₂	-141.22				
-CONH-	-128.12				
*-NHCO-	-158.39				
-CON<	87.92				
-NO₂	11.51	45.55	4.77	4.65	-14.57
*-NO₂	18.00	45.64	4.61	4.61	-14.65
-ONO-	20.68	54.85	10.34	6.32	-16.08
-ONO₂	-36.72	72.43	17.25	31.86	-29.14
-NCS	234.46	61.55			

Table 6-2f Corrections for Type-Number and Multiple Substitutions

Functional Group	ΔH	ΔS	Δa	Δb	Δc
=O (aldehyde)	-22.69	18.84	-3.60	6.74	-4.81
=O (ketone)	-13.82	30.94	6.66	-47.31	34.37
-OH	-11.10	0.84	0.42	0.00	-0.42
-O-	-9.55	-2.30	2.14	-5.02	3.31
*-O-	-11.76	-2.51	2.09	-5.02	3.35

groups (not hydrogen atoms). Functional groups are of three general types characterized by one, two, or three bonds. Examples are $-Br$, $-O-$, $>N-$. In the first case, the $-Br$ substitutes for a $-CH_3$; in the second, the $-O-$ replaces a $-CH_2-$; and in the third, the $>N-$ replaces a $>CH-$. An aldehyde or ketone group ($=O$) replaces two $-CH_3$ groups. Values for such *fundamental contributions* are shown in Table 6-2e.

TABLE 6-2   Yoneda Group Contributions for Ideal-Gas Properties[a]
(*Continued*)

Table 6-2f   Corrections for Type-Number and Multiple Substitutions (continued)

Functional Group	Δ_H	Δ_S	Δ_a	Δ_b	Δ_c
-OOH	8.37				
-OO-	-10.47				
-COOH	6.45	35.92	0.00	0.00	0.00
←-COO-	-5.07	35.92	0.00	0.00	0.00
←-OOC-	-11.72	-2.50	2.09	-5.02	3.35
*-COO-	7.49	-2.51	2.09	-5.02	3.35
-COOCO-	-5.07	36.01	0.00	0.00	0.00
-COO₂CO-	-21.35				
-OOCH	33.45	-2.51	2.09	-5.02	3.35
-CO₃-	-1.21				
-F	-6.15	4.14	1.59	-0.54	1.59
-F,-F	-15.37	-3.81	-2.01	-0.75	-1.76
-F,-Cl	11.01	-0.67	7.20	-13.98	18.34
-F,-Br	17.54	6.82	4.14	-16.79	4.40
-F,-I	17.25	-0.38	7.03	-6.49	4.23
-COF	1.67				
-Cl	-2.60	5.19	3.77	-12.56	8.04
-Cl,-Cl	17.79	-6.24	-2.60	6.49	-3.77
-Cl,-Br	21.52	6.20	7.24	-29.10	12.64
-Cl,-I	20.52	5.19	7.03	-27.59	18.92
-COCl	1.88				
-Br	-7.24	-5.23	1.63	-26.59	9.67
-Br,-Br	17.63	9.92	4.69	-35.96	19.68
-Br,-I	20.52	7.95	-1.59	-32.41	16.08
-COBr	1.67				
-I	-4.31	3.94	2.76	-10.13	7.29
-I,-I	23.40	-3.06	0.50	0.75	-1.51
-COI	1.67				
-SH	-1.13	1.59	1.47	-1.21	-1.59
-S-	-3.56	-0.17	-0.17	4.52	-3.77
*-S-	-1.17	-0.42	-0.42	4.61	-3.77
-SS-	-3.43	0.08	-1.76	11.14	-9.59
-SO-	-8.25				
*-SO-	-8.37				

There are, in addition, two further contributions which may be necessary when nonhydrocarbons are synthesized. These are termed *corrections,* and they are shown in Table 6-2*f.*

1. *Type number corrections.* These corrections are never necessary if a functional group is attached to an aromatic ring, e.g., when −Cl replaces −CH₃ in toluene to form chlorobenzene. In other cases, the general rules to follow are:

- Make *all* substitutions of functional groups first.

Table 6-2f   Corrections for Type-Number and Multiple Substitutions (continued)

Functional Group	Δ_H	Δ_S	Δ_a	Δ_b	Δ_c
-SO2-	-1.13				
*-SO2-	25.87				
-SO3H	-11.72				
-OSO2-	-11.76				
-OSO3-	-10.76				
-NH2	-5.44	-1.42	0.67	1.97	-2.55
-NH-	-9.76	-1.26	0.84	2.09	-2.51
*-NH-	-8.71	-1.26	0.84	2.09	-2.51
-N<	-7.12	-1.26	0.84	2.09	-2.51
*-N<	-4.19	-1.26	0.84	2.09	-2.51
+=N-	0.84				
+-N=	-3.77				
-N=N-	-3.77				
-NHNH2	-5.44	-1.26			
-N(NH2)-	-5.44	-1.26			
*-N(NH2)-	-5.44				
-NHNH-	-5.44	-1.26			
*-NHNH-	-5.44				
-CN	-12.90	2.34	4.27	-20.43	18.76
-NC	-12.98	2.51	4.19	-20.52	18.84
=NOH	0.84				
-CONH2	0.13	36.01	0.00	0.00	0.00
+-CONH-	-5.02				
+-NHCO-	-9.63				
*-NHCO-	-5.02				
-NO2	-9.46	0.00	0.00	0.00	0.00
-ONO-	-26.54	0.00	0.00	0.00	0.00
-ONO2	-10.34	2.76	-1.55	3.43	-2.30
-NCS	-3.77	-1.26			

a.   Values of Δ_H are used to estimate the enthalpy of formation at 298 K in kJ/mol; values of Δ_S are used to estimate the entropy in the ideal-gas state at one atmosphere and 298 K in J/mol K; values of Δ_a, Δ_b, and Δ_c are used to estimate the ideal-gs heat capacity in Eq. (6-4.3) in J/mol K.

The symbol * indicates an aromatic nucleus; the symbol + indicates the directionality of the bond when making type-number corrections.

■ For *each* functional group, focus on the carbon atoms bonded to the functional group. For each bonded carbon, count the number of adjacent, bonded atoms other than hydrogen. The sum is the multiplier for the type number correction in Table 6-2f. If the functional group has multiple bonds, this procedure is repeated for each *single* bond. For example, consider 1-chloropropane. Here the −Cl is attached to a carbon which itself has only a single non-

hydrogen atom attached. Thus, only one type number correction is applied for $-Cl$ in Table 6-2f. For 2-chloropropane, there would be two type number corrections for the $-Cl$. For methyl ethyl ketone, the $=O$ is bonded to a carbon which itself is connected to two other carbons. Thus the number of type number corrections for the $=O$ is two. Finally, for perfluoroethane, each fluorine is bonded to a carbon which is attached to three other nonhydrogen atoms. With six $-F$, each with three type number corrections, the total number of type number corrections for $-F$ in Table 6-2f is $3 \times 6 = 18$.

2. *Multiple corrections.* If certain functional groups should be connected to the *same* carbon atom, corrections given in Table 6-2f are necessary. For example, with 1,1,1-trichloroethane, there would be three $-Cl, -Cl$ multiple-bond corrections to account for the three binary interactions between the chlorine atoms.

We illustrate Yoneda's method in Example 6-2. Calculated values of ΔH_f° (298 K), S° (298 K), and C_p° (T) are compared with literature values in Tables 6-7, 6-8, and 6-6, respectively. A comparison of the reliability of the method in comparison with others is discussed in Sec. 6-8.

Example 6-2 By using Yoneda's method, estimate ΔH_f° (298 K), S° (298 K), and C_p° (800 K) for isopropyl ether. The literature values are -319.0 kJ/mol, 390.5 J/(mol·K), and 311.5 J/(mol·K) [25].

solution The synthesis strategy is to form 2,4-dimethylpentane and then insert the functional group $-O-$ for the number 3 carbon atom $(-CH_2-)$. The base group is methane.

	Δ_H	Δ_S	Δ_a	Δ_b	Δ_c
Base group → methane	-74.90	186.31	16.71	65.65	-9.96
Primary methyl:					
Substitution → ethane	-9.84	43.33	-9.92	103.87	-43.54
Secondary methyl:					
Substitutions					
A=1, B=1 → propane	-21.10	43.71	-3.68	98.22	-42.29
A=1, B=2 → n-butane	-20.60	38.90	1.47	81.48	-31.48
A=1, B=2 → n-pentane	-20.60	38.90	1.47	81.48	-31.48
A=2, B=2 → 2-methylpentane	-26.59	27.34	-0.63	90.73	-37.56
A=2, B=2 → 2,4-dimethylpentane	-26.59	27.34	-0.63	90.73	-37.56
Fundamental contribution:					
$-O-$ → isopropyl ether	-85.54	-5.28	13.27	-85.37	38.60
Type number correction:					
$-O-$ four times	-38.20	-9.20	8.56	-20.08	13.24
	-323.96	391.35	26.62	506.71	-182.03

With Eqs. (6-4.1) to (6-4.3)

ΔH_f° (298 K) $= -323.96$ kJ/mol

Difference $= -323.96 - (-319.0) = -4.9$ kJ/mol

S° (298 K) $= 391.35$ J/(mol·K)

difference $= 391.35 - 390.5 = 0.9$ J/(mol·K)

$$C_p^\circ \ (800 \text{ K}) = 26.62 + (506.71)\left(\frac{800}{1000}\right) - (182.03)\left(\frac{800}{1000}\right)^2$$

$$= 315.5 \text{ J/(mol·K)}$$

$$\text{Error} = \frac{315.5 - 311.5}{311.5} \times 100 = 1.3\%$$

6-5 Method of Thinh et al. [26, 27]

An additive group method for estimating ΔH_f° (298 K), ΔG_f° (298 K), S° (298 K), and C_p° (T) for *hydrocarbons* employs the following equations:

$$\Delta H_f^\circ \ (298 \text{ K}) = \sum_j n_j \, \Delta_H \tag{6-5.1}$$

$$\Delta G_f^\circ \ (298 \text{ K}) = \sum_j n_j \, \Delta_G \tag{6-5.2}$$

$$S^\circ \ (298 \text{ K}) = \sum_j n_j \, \Delta_S \tag{6-5.3}$$

$$C_p^\circ \ (T) = \sum_j n_j \left[A + B_1 \exp\left(\frac{-C_1}{T^{n_1}}\right) - B_2 \exp\left(\frac{-C_2}{T^{n_2}}\right) \right] \tag{6-5.4}$$

Values of Δ_H, Δ_G, Δ_S, A, B_1, B_2, C_1, C_2, n_1, and n_2 are shown in Table 6-3 for many hydrocarbon groups. Equation (6-5.4) is a modified form suggested earlier by Yuan and Mok [30]. It is sometimes inconvenient to use because it cannot be integrated analytically and numerical techniques must be employed.

This method is illustrated in Example 6-3, and estimated values of the ideal-gas properties are compared to literature values in Tables 6-6 through 6-9. It is compared with other estimation methods in Sec. 6-8.

Example 6-3 Estimate the heat capacity of 2-methyl-1,3-butadiene at 800 K and the enthalpy of formation at 298 K by using the group contribution method suggested by Thinh and his coworkers. The literature values for these two properties are 201.0 J/(mol·K) and 75.78 kJ/mol, respectively [25].

solution 2-Methyl-1,3-butadiene may be broken down to $-CH_3$, $-HC=CH_2$, and $>C=CH_2$. With Table 6-3, for this compound,

$$\Delta H_f^\circ = -42.36 + 55.12 + 67.81 = 80.54 \text{ kJ/mol}$$

Difference = estimated $-$ literature $= 80.54 - 75.78 = 4.8$ kJ/mol

TABLE 6-3 Thinh et al., Group Contributions for Ideal-Gas Properties

GROUP	Δ_H	Δ_S	Δ_G	A	B_1	C_1	n_1	B_2	C_2	n_2
-CH3	-42.362	114.823	-16.454	19.8312	85.5824	1013.8229	1.0489	0	0	0
-CH2-	-20.641	38.979	8.374	12.9037	573.0482	788.7739	1.0380	503.6800	832.8313	1.0452
>CH-	-7.519	-49.634	28.428	-2.6017	318.1767	601.8911	0.9953	256.7467	1013.8229	1.0489
>C<	3.358	-152.693	50.576	-10.3372	375.4710	733.9538	1.0396	342.3287	1013.8229	1.0489
=CH2	26.159	109.799	34.085	14.3951	64.4428	527.1308	0.9644	0	0	0
≡C-	114.467	32.9773	105.687	10.4586	100.8906	1133.5426	1.0774	85.5824	1013.8229	1.0489
≡CH	113.450	100.4769	104.670	6.9241	52.1081	21.3585	0.5	0	0	0
=C=	139.940	24.49	134.346	6.4087	152.4962	321.4962	0.9048	128.8860	527.1308	0.9644
-HC=CH2	55.119	139.46	75.383	6.9526	131.7946	134.8699	0.8030	0	0	0
>C=CH2	67.809	64.14	91.021	20.6066	262.0187	652.9594	0.9990	171.1643	1013.8229	1.0489
>C=C<	102.836	-96.42	134.982	-0.0063	430.5353	511.5828	0.9573	342.3287	1013.8229	1.0489
>C=CH-	84.506	-5.67	109.066	11.0372	329.0795	874.4157	1.0464	256.7467	1013.8229	1.0489
-HC=CH-(cis)	77.732	71.38	98.808	13.3291	260.7753	1110.9532	1.0843	171.1643	1013.8229	1.0489
-HC=CH-(trans)	73.545	67.03	95.920	24.7813	252.2304	990.4639	1.0590	171.1643	1013.8229	1.0489
>C=C=CH2	214.515	90.23	231.656	31.4039	279.1155	578.8631	0.9870	171.1643	1013.8229	1.0489
-HC=C=CH2	204.684	178.38	215.034	35.8315	208.9812	700.3515	1.0163	85.5824	1013.8229	1.0489
-HC=C=CH-	223.307	95.25	238.982	33.7481	270.4279	949.4988	1.0596	171.1643	1013.8229	1.0489
HC↔	13.8303	44.8963	21.6240	6.0060	45.5189	1174.9378	1.1387	0	0	0
-C↔	23.2422	-19.3501	30.7052	5.7087	333.3065	1269.0479	1.1387	313.6947	986.1985	1.0928
↔C↔	18.7849	-10.6483	23.6500	9.7540	199.4973	1587.2948	1.1915	182.0760	1174.9378	1.1387

Note: ↔ indicates that the carbon is bonded to other carbons in an aromatic ring

GROUP	ΔH	ΔS	ΔG	A	B₁	C₁	n₁	B₂	C₂	n₂
RING FORMATION CORRECTIONS										
3-membered ring	103.117	129.9386	64.393	-7.2109	126.0424	4304.6037	1.3222	137.8135	1237.7501	1.1173
5-mem.ring-cyclopentane	25.916	98.18	-3.224	-23.2619	364.2466	1281.9257	1.1221	346.3003	545.5184	0.9912
5-mem.ring-cyclopentene	17.141	101.53	-13.063	-9.8327	295.5738	1877.9329	1.1852	295.5236	813.0059	1.0604
5-mem.ring-cyclohexane	0.628	64.56	-18.464	-7.8410	400.4109	4371.2289	1.3210	415.5604	545.5184	0.9912
6-mem.ring-cyclohexene	-2.286	83.65	-27.130	-19.9091	381.0306	972.7163	1.1001	364.4877	756.9254	1.0481
BRANCHING IN FIVE-MEMBERED RINGS										
Single branching	0.234	20.85	-6.448	11.2315	430.9482	1040.8363	1.0906	438.4517	1062.1344	1.1013
Double branching										
1,1	-2.604	14.03	-6.783	23.0044	482.8142	1362.2334	1.1394	511.9707	951.9636	1.0909
1,2 (cis)	6.146	20.89	-0.084	21.7090	488.0603	1170.5749	1.1148	511.9707	951.9636	1.0909
1,2 (trans)	-1.013	21.56	-7.452	21.0747	490.8382	1084.4398	1.1022	511.9707	951.9636	1.0909
1,3 (cis)	-0.176	21.56	-6.615	21.0747	490.8382	1084.4398	1.1022	511.9707	951.9636	1.0909
1,3 (trans)	2.085	21.56	-4.354	21.0747	490.8382	1084.4398	1.1022	511.9707	951.9636	1.0909

TABLE 6-3 Thinh et al., Group Contributions for Ideal-Gas Properties (*Continued*)

GROUP	Δ_H	Δ_S	Δ_G	A	B_1	C_1	n_1	B_2	C_2	n_2
BRANCHING IN SIX-MEMBERED RINGS										
Single branching	-2.412	18.92	-8.080	6.5147	472.5457	2470.4850	1.2344	473.6389	3061.5552	1.2706
Double branching										
1,1	0.578	14.40	-3.726	18.9943	521.8143	3819.4942	1.3044	546.4984	2405.6012	1.2375
1,2 (cis)	9.412	23.91	-2.261	15.2973	530.8527	2640.9182	1.2462	546.4984	2405.6012	1.2375
1,2 (trans)	1.583	20.31	-4.480	12.5169	536.5874	2189.0807	1.2193	546.4984	2405.6012	1.2375
1,3 (cis)	-3.190	19.85	-9.127	19.7734	527.3798	3032.2880	1.2661	546.4984	2405.6012	1.2375
1,3 (trans)	5.016	25.62	-2.638	16.1489	533.1098	2403.6929	1.2294	546.4984	2405.6012	1.2375
1,4 (cis)	4.932	19.85	-1.005	16.1489	533.1098	2403.6929	1.2294	546.4984	2405.6012	1.2375
1,4 (trans)	-3.023	14.19	-7.243	14.5722	530.9130	2616.9819	1.2473	546.4984	2405.6012	1.2375
CORRECTIONS FOR BRANCHING IN AROMATICS										
Double branching										
1,2	1.926	17.54	7.159	9.2562	390.1846	1137.6065	1.1076	393.0425	1381.8801	1.1442
1,3	0.167	-12.60	3.927	1.7204	394.2571	1266.8220	1.1287	393.0425	1381.8801	1.1442
1,4	0.879	-17.88	6.217	4.4970	390.6682	1414.2979	1.1428	393.0425	1381.8801	1.1442
Triple branching										
1,2,3	6.280	-29.64	15.127	13.5058	446.9279	1416.3668	1.1311	452.4386	1496.1894	1.1513
1,2,4	1.926	-24.49	9.236	15.8357	442.3262	1513.4331	1.1414	452.4386	1496.1894	1.1513
1,3,5	-0.209	-35.29	10.325	5.9959	450.0936	1482.6086	1.1443	452.4386	1496.1894	1.1513

SPECIAL CORRECTIONS FOR FIRST FEW (-CH₂-) IN NORMAL SERIES

GROUP	ΔH	ΔS	ΔG	A	B_1	C_1	n_1	B_2	C_2	n_2
For the first three -CH₂- in normal paraffins										
first -CH₂-	1.45	1.47	1.03	-6.7303	248.7780	653.8562	0.9992	242.1603	779.2506	1.0174
first and second -CH₂-	-0.23	2.72	-1.01	-2.4878	310.2695	745.5631	1.0220	312.2675	694.6245	1.0053
first and second and third -CH₂-	0.11	2.60	-0.59	-1.3214	376.7655	750.0491	1.0256	382.0195	652.7659	0.9996
For the first three (-CH₂-) in normal alkyl benzenes										
first -CH₂-	0.42	1.76	-0.08	-2.6088	405.3002	972.3475	1.0980	401.3810	1115.4125	1.1162
first and second -CH₂-	-0.92	3.02	-1.77	3.8192	463.3222	1065.8703	1.1084	469.7326	1014.5118	1.0997
first and second and third -CH₂-	-1.93	2.89	-2.71	4.9593	529.7412	1024.6444	1.1005	538.2738	943.4540	1.0870
For the first two (-CH₂-) in normal monoolefins										
first -CH₂-	7.758	12.54	4.250	7.8264	268.1097	616.9205	0.9973	287.2903	313.8732	0.8983
first and second -CH₂-	7.591	13.80	3.705	12.6199	328.8149	721.9341	1.0225	355.8680	352.8265	0.9180
For the first two (-CH₂-) in normal acetylenes										
first -CH₂-	0.38	3.77	-0.054	-8.1701	226.4510	333.3507	0.9005	209.3387	504.9147	0.9628
first and second -CH₂-	0.17	3.77	-0.641	-1.0002	280.4281	533.4160	0.9750	278.6772	510.4336	0.9686

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TABLE 6-3 Thinh et al., Group Contributions for Ideal-Gas Properties (*Continued*)

GROUP	Δ_H	Δ_S	Δ_G	A	B_1	C_1	n_1	B_2	C_2	n_2
For the first –CH₂– outside the ring, in normal alkyl cyclopentanes										
first –CH₂–	0.251	-0.54	0.460	-30.4929	587.9033	312.1951	0.9010	499.7695	956.9970	1.0777
For the first two –CH₂– outside the ring, in normal alkyl cyclohexanes										
first –CH₂–	3.642	0.29	3.601	0.8016	536.6820	2165.9117	1.2143	539.4721	2097.6983	1.2081
first and second –CH₂–	2.721	-1.72	3.308	-2.1981	615.9164	1465.2225	1.1521	606.7502	1839.8190	1.1870
CORRECTIONS FOR BRANCHING IN PARAFFIN CHAINS										
side chain with two or more C atoms	6.699	-0.21	6.573	0	0	0	0	0	0	0
three adjacent –CH₂– groups	-12.460	29.35	19.510	0	0	0	0	0	0	0
adjacent >HC–C<– groups	10.986	11.72	7.536	0	0	0	0	0	0	0

For C_p°, one cannot add the contributions for A, B_1, etc., but rather, each group must be evaluated separately. At 800 K,

$$-CH_3 = 19.8312 + 85.5824 \exp \frac{-1013.8229}{(800)^{1.0489}} = 54.15$$

$$-HC{=}CH_2 = 6.9526 + 131.7946 \exp \frac{-134.8699}{(800)^{0.8030}} = 77.21$$

$$>C{=}CH_2 = 20.6066 + 262.0187 \exp \frac{-652.9594}{(800)^{0.9990}}$$

$$- 171.1643 \exp \frac{-1013.8229}{(800)^{1.0489}} = 67.19$$

$$C_p^\circ \,(800\ K) = 54.15 + 77.21 + 67.19 = 198.55\ J/(mol\cdot K)$$

$$\text{Error} = \frac{198.55 - 201.0}{201.0} \times 100 = -1.2\%$$

6-6 Method of Benson

For the estimation of ΔH_f° (298 K), S° (298 K), and C_p° (T), an accurate group contribution method was developed by Benson and his colleagues. It is thoroughly described in a book [3] and in a comprehensive review [5]. Contributions are given only for atoms with valences greater than unity. For each group, the key atom is given but followed by a notation specifying other atoms bonded to the key atom. For example, $C-(C)(H)_3$ refers to a carbon atom bonded to another carbon and three hydrogens, that is, $-CH_3$. The contributions for this method are shown in Table 6-4.

To employ this technique, one must become acquainted with the shorthand notation introduced; for example, C_d refers to a carbon atom which also participates in a double bond with another carbon atom; it is assumed to have a valence of 2. Notes at the bottoms of the tables define terms which are not immediately obvious.

Table 6-4 is in a continual state of change as new groups are added and older values are updated [9, 18, 22, 23]. It has been adapted for computer use [16, 19], and many new values were added by Shell Development Co. [8] and Olson [17].

Bures et al. [6] have attempted to fit the tabular values of C_p° presented by Benson with various equation forms. In many tests of Bures et al.'s equations, it was found that the calculated group values of C_p° agreed well with Benson's tabulated values. In other cases, however, serious errors were noted; thus, Bures et al.'s equations are not given.

Corrections for symmetry

When determining S° (298 K) by the Benson group contribution method, one must make corrections for molecular symmetry.

TABLE 6-4 Benson Group Contributions to Ideal-Gas Properties

GROUP	$\Delta H_f^{\,o}$(298 K) kJ/mol	$S^{\,o}$(298 K) J/mol K	$C_p^{\,o}$, J/mol K 300 K	400 K	500 K	600 K	800 K	1000 K
			Hydrocarbon Groups					
$C-(C)(H)_3$	−42.20	127.32	25.92	32.82	39.36	45.18	54.51	61.84
$C-(C)_2(H)_2$	−20.72	39.44	23.03	29.10	34.54	39.15	46.35	51.67
$C-(C)_3(H)$	−7.95	−50.53	19.01	25.12	30.02	33.70	38.98	42.08
$C-(C)_4$	2.09	−146.96	18.30	25.67	30.81	34.00	36.72	36.68
$C_d-(H)_2$	26.21	115.60	21.35	26.63	31.44	35.59	42.16	47.19
$C_d-(C)(H)$	35.96	33.37	17.42	21.06	24.33	27.21	32.03	35.38
$C_d-(C)_2$	43.29	−53.17	17.17	19.30	20.89	22.02	24.28	25.46
$C_d-(C_d)(H)$	28.39	26.71	18.67	24.24	28.26	31.07	34.96	37.64
$C_d-(C_d)(C)$	37.18	−61.13	(18.42)	(22.48)	(24.83)	(25.87)	(27.21)	(27.72)
$C_d-(C_d)_2$	19.26							
$C_d-(C_B)(H)$	28.39	26.80	18.67	24.24	28.26	31.07	34.96	37.64
$C_d-(C_B)(C)$	36.17	(−61.13)	(18.42)	(22.48)	(24.83)	(25.87)	(27.21)	(27.72)
$C_d-(C_B)_2$	33.49							
$C_d-(C_t)(H)$	28.39	26.80	18.67	24.24	28.26	31.07	34.96	37.64
$C_d-(C_t)(C)$	35.71		18.42	22.48	24.83	25.87	27.21	27.72
$C-(C_d)(H)_3$	−42.20	127.32	25.92	32.82	39.36	45.18	54.51	61.84
$C-(C_d)_2(H)_2$	−17.96	(42.71)	(19.68)	(28.47)	(35.17)	(40.14)	(47.31)	(52.75)
$C-(C_d)_2(C)_2$	4.86		14.95	25.04	31.44	35.04	37.68	37.76
$C-(C_d)(C)_3$	7.03	(−145.37)	16.71	(25.29)	(31.11)	(34.58)	(37.35)	(37.51)
$C-(C_d)(C)(H)_2$	−19.93	41.03	22.69	28.72	34.83	39.73	46.98	52.25
$C-(C_d)_2(C)(H)_2$	−6.20	(−48.99)	(17.42)	(24.74)	(30.73)	34.29	(39.61)	(42.66)
$C-(C_d)_2(C)(H)$	−5.19		15.66	24.49	30.65	34.75	39.94	43.17

			$C_p°$, J/mol K					
GROUP	$\Delta H_f°(298\ K)$ kJ/mol	$S°(298\ K)$ J/mol K	300 K	400 K	500 K	600 K	800 K	1000 K
Hydrocarbon Groups (continued)								
$C-(C_t)(H)_3$	-42.20	127.32	25.92	32.82	39.36	45.18	54.51	61.84
$C-(C_t)(C)(H)_2$	-19.80	43.12	20.72	27.47	33.20	38.02	45.47	51.04
$C-(C_t)(C)_2(H)$	-7.20	(-46.89)	(16.71)	(23.49)	(28.68)	(32.57)	(38.10)	(41.45)
$C-(C_B)(H)_3$	-42.20	127.32	25.92	32.82	39.36	45.18	54.51	61.84
$C-(C_B)(C)(H)_2$	-20.35	38.94	24.45	31.86	37.60	41.91	48.11	52.50
$C-(C_B)(C)_2(H)$	-4.10	(-51.08)	(20.43)	(27.88)	(33.08)	(36.63)	(40.74)	(42.91)
$C-(C_B)(C)_3$	11.76	(-147.29)	(18.30)	(28.43)	(33.87)	(36.76)	(38.48)	(37.51)
$C-(C_B)_2(C)(H)$	-5.19		15.66	24.49	30.65	34.75	39.94	43.17
$C-(C_B)_2(C)_2$	-4.86		14.95	25.04	31.44	35.04	37.68	37.76
$C-(C_B)_2(C_d)(H)_2$	-17.96	(42.71)	(19.68)	(28.47)	(35.17)	(40.19)	(47.31)	(52.75)
$C_t-(H)$	112.75	103.41	22.06	25.08	27.17	28.76	31.28	33.33
$C_t-(C)$	115.35	26.59	13.10	14.57	15.95	17.12	19.26	20.60
$C_t-(C_d)$	122.25	(26.92)	(10.76)	(14.82)	(14.65)	(20.60)	(22.36)	(23.03)
$C_t-(C_B)$	(122.25)	26.92	10.76	14.82	14.65	20.60	22.36	23.03
$C_B-(H)$	13.82	48.27	13.57	18.59	22.86	26.38	31.57	35.21
$C_B-(C)$	23.07	-32.20	11.18	13.15	15.41	17.38	20.77	22.78
$C_B-(C_d)$	23.78	-32.66	15.03	16.62	18.34	19.76	22.11	23.49
$C_B-(C_t)$	23.86	-32.66	15.03	16.62	18.34	19.76	22.11	23.49
$C_B-(C_B)$	20.77	-36.17	13.94	17.67	20.47	22.06	24.12	24.91
C_a	143.19	25.12	16.33	18.42	19.68	20.93	22.19	23.03
$C_{BF}-(C_b)_2(C_{BF})$	20.10	-20.93	12.52	15.32	17.67	19.43	21.90	23.24
$C_{BF}-(C_B)(C_{BF})_2$	15.49	-20.93	12.52	15.32	17.67	19.43	21.90	23.24
$C_{BF}-(C_{BF})_3$	6.07	7.62	8.71	11.93	14.65	16.87	19.89	21.52

TABLE 6-4 Benson Group Contributions to Ideal-Gas Properties (*Continued*)

GROUP	ΔH$_f$°(298 K) kJ/mol	S°(298 K) J/mol K	C_p°, J/mol K 300 K	400 K	500 K	600 K	800 K	1000 K
			Next-Nearest-Neighbor Correction					
Alkane gauche	3.35							
Alkene gauche	2.09							
Cis	4.19^c	d	-5.61	-4.56	-3.39	-2.55	-1.63	-1.09
Ortho	2.39	-6.74	4.69	5.65	5.44	4.90	3.68	2.76
Ring (σ)^{e,f}			Corrections to be Applied for Ring Compounds					
Cyclopropane (6)	115.56	134.40	-12.77	-10.59	-8.79	-7.95	-7.41	-6.78
Cyclopropene (2)	224.83	140.68						
Cyclobutane (8)	109.69	124.77	-19.30	-16.29	-13.15	-11.05	-7.87	-5.78
Cyclobutene (2)	124.77	121.42	-10.59	-9.17	-7.91	-7.03	-6.20	-5.57
Cyclopentane (10)	26.38	114.30	-27.21	-23.03	-18.84	-15.91	-11.72	-7.95
Cyclopentene (2)	24.70	108.02	-25.04	-22.40	-20.47	-17.33	-12.27	-9.46
Cyclopentadiene	25.12	117.23	-18.00					
Cyclohexane (6)	0	78.71	-24.28	-17.17	-12.14	-5.44	4.61	9.21
Cyclohexene (2)	5.86	90.02	-17.92	-12.73	-8.29	-5.99	-1.21	0.33
Cycloheptane (1)	26.80	66.57						
Cyclooctane (8)	41.45	69.08						
Naphthalene	--	33.91						

GROUP	ΔHf°(298 K) kJ/mol	S°(298 K) J/mol K	Cp°, J/mol K					
			300 K	400 K	500 K	600 K	800 K	1000 K
		Oxygen-Containing Compounds						
$CO-(CO)(H)$	-108.86		28.14	32.78	37.26	41.41	47.86	50.74
$CO-(CO)(C)$	-122.25		22.86	26.46	29.98	32.95	37.68	40.86
$CO-(O)(C_d)$	-136.07		25.00	28.05	31.02	33.58	37.14	39.19
$CO-(O)(C_B)$	-136.07	20.01	9.13	11.51	16.66	21.06	26.33	29.56
$CO-(O)(C)$	-146.96	146.24	25.00	28.05	30.98	33.58	37.14	39.19
$CO-(C_d)(H)$	-134.40		29.43	32.95	36.93	40.53	46.72	51.08
$CO-(C_d)(C)$	-132.72		29.43	32.95	36.93	40.53	46.72	51.08
$CO-(C_B)(C)$	-159.52		22.02	28.34	32.11	35.50	40.28	41.24
$CO-(C_B)(C)$	-129.37		23.78	28.97	32.24	35.00	39.31	40.86
$CO-(C_B)(H)$	-144.86	62.84	26.80	32.32	37.30	41.24	48.11	50.62
$CO-(C)_2$	-131.47	146.24	23.40	26.46	29.68	32.49	37.22	40.24
$CO-(C)(H)$	-121.84	224.71	29.43	32.95	36.93	40.53	46.72	51.08
$CO-(H)_2$	-108.86		35.46	39.27	43.79	48.23	55.98	62.01
$O-(C_B)(CO)$	-136.07		8.62	11.30	13.02	14.32	16.24	17.50
$O-(CO)_2$	-213.11	35.13	-1.72	7.45	13.40	16.75	21.48	24.49
$O-(CO)(O)$	-79.55	102.66	15.49	15.49	15.49	15.49	17.58	17.58
$O-(CO)(C_d)$	-196.36	(39.36)	6.03	12.48	16.66	18.80	20.81	21.77
$O-(CO)(C)$	-185.48	(39.36)	16.33	15.11	17.54	19.34	20.89	20.18
$O-(CO)(H)$	-243.25	116.60	15.95	20.85	24.28	26.54	30.10	32.45
$O-(O)(C)$	(-18.84)	42.29	(15.49)	(15.49)	(15.49)	(15.49)	(17.58)	(17.58)
$O-(O)_2$	(-79.55)	40.61	(15.49)	(15.49)	(15.49)	(15.49)	(17.58)	(17.58)
$O-(O)(H)$	-68.12		21.65	24.24	26.29	27.88	29.94	31.44
$O-(C_d)(C)$	-137.33		14.24	15.49	15.49	15.91	18.42	19.26
$O-(C_d)(C)$	-133.56		14.24	15.49	15.49	15.91	18.42	19.26
$O-(C_B)_2$	-88.34		4.56	5.11	6.28	8.33	11.93	14.70
$O-(C_B)(C)$	-94.62		14.24	15.49	15.49	15.91	18.42	19.26
$O-(C_B)(H)$	-158.68	121.84		18.84	20.10	21.77	25.12	27.63

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TABLE 6-4   Benson Group Contributions to Ideal-Gas Properties *(Continued)*

GROUP	$\Delta H_f^\circ(298\text{ K})$ kJ/mol	$S^\circ(298\text{ K})$ J/mol K	C_p°, J/mol K 300 K	400 K	500 K	600 K	800 K	1000 K
			Oxygen-containing Compounds, continued					
$O-(C)_2$	-99.23	36.34	14.24	15.49	15.49	15.91	18.42	19.26
$O-(C)(H)$	-158.68	121.71	18.13	18.63	20.18	21.90	25.20	27.67
$C_d-(CO)(O)$	37.68		23.40	29.31	31.32	32.45	33.58	34.04
$C_d-(CO)(C)$	39.36		15.62	18.76	21.02	22.61	24.91	26.67
$C_d-(CO)(H)$	35.59		15.87	20.52	24.45	27.80	32.66	36.59
$C_d-(O)(C_d)$	37.26		(18.42)	(22.48)	(24.83)	(25.87)	(27.21)	(27.72)
$C_d-(O)(C)$	43.12		17.17	19.30	20.89	22.02	24.28	25.46
$C_d-(O)(H)$	36.01		17.42	21.06	24.33	27.21	32.03	35.38
$C_B-(CO)$	40.61		11.18	13.15	15.41	17.38	20.77	22.78
$C_B-(O)$	-3.77	-42.71	16.33	22.19	25.96	27.63	28.89	28.89
$C-(CO)_2(H)_2$	-31.82		23.45	29.52	35.13	40.53	48.48	53.88
$C-(CO)(C)_2(H)$	-7.54	-50.24	26.00	31.65	33.49	34.37	38.43	40.32
$C-(CO)(C)(H)_2$	-21.77	40.19	25.96	32.24	36.43	39.77	46.47	51.08
$C-(CO)(C)_3$	6.70		21.23	28.81	32.70	34.62	36.84	36.09
$C-(CO)(H)_3$	-42.29	127.32	25.92	32.82	39.36	45.18	54.51	61.84
$C-(O)_2(C)_2$	-77.87		6.66	16.54	25.96	30.94	31.90	35.50
$C-(O)_2(C)(H)$	-68.24		21.19	30.48	37.81	39.40	43.17	45.01
$C-(O)_2(H)_2$	-63.22		11.85	21.19	31.48	38.18	43.21	47.27
$C-(O)(C_B)(H)_2$	-33.91	40.61	15.53	26.25	34.67	40.99	49.36	55.27
$C-(O)(C_B)(C)(H)$	-25.46		21.52	30.56	36.97	39.48	42.83	44.38
$C-(O)(C_d)(H)_2$	-28.89		19.51	29.18	36.22	41.37	48.32	53.30
$C-(O)(C)_3$	-27.63	-140.51	18.13	25.92	30.35	32.24	34.33	34.50
$C-(O)(C)_2(H)$	-30.14	-46.05	20.10	27.80	33.91	36.55	41.07	43.54
$C-(O)(C)(H)_2$	-33.91	41.03	20.89	28.68	34.75	39.48	46.52	51.62
$C-(O)(H)_3$	-42.29	127.32	25.92	32.82	39.36	45.18	54.55	61.84

GROUP	ΔH_f°(298 K) kJ/mol	S°(298 K) J/mol K	$C_p°$, J/mol K					
			300 K	400 K	500 K	600 K	800 K	1000 K
			Strain and Ring Corrections for Oxygen-containing Compounds					
Ether oxygen, gauche	1.3		-0.42	-3.73	-4.61	-3.06	-2.51	-0.96
Ditertiary ethers	32.7		-16.50	-23.61	-29.94	-36.97	-50.41	-62.38
Ethylene oxide	115.6	131.5	-8.4	-11.7	-12.6	-10.9	-9.6	-9.6
Trimethylene oxide	110.5	116.0	-19.3	-20.9	-17.6	-14.7	-10.9	0.8
Tetrahydrofuran	28.1		-17.8	-19.01	-17.04	-14.86	-12.94	-10.93
Tetrahydropyran	9.2		-17.92	-12.73	-8.29	-5.99	-1.21	0.33
1,3-Dioxane	3.8		-10.51	-12.06	-9.55	-6.24	-1.09	2.34
1,4-Dioxane	22.6		-17.42	-19.13	-13.02	-7.87	-4.56	-1.97
1,3,5-Trioxane	21.4		7.49	2.34	-2.55	-2.72	-5.02	-10.17
Furan	-24.3		-17.54	-15.20	-12.23	-10.01	-8.33	-7.20
Dihydropyran	5.0		-18.59	-13.40	-6.53	-1.88	1.76	2.76
Cyclopentanone	21.8		-35.71	-30.10	-22.23	-15.57	-9.46	-5.11
Cyclohexanone	9.2		-33.91	-27.51	-17.75	-8.00	2.93	8.25
Succinic anhydride	18.8		-33.08	-25.20	-17.80	-14.99	-14.03	-12.81
Glutaric anhydride	3.3		-33.20	-25.29	-18.84	-15.03	-14.03	-12.85
Maleic anhydride	15.1		-21.44	-14.15	-8.46	-9.17	-1.55	-0.04

TABLE 6-4 Benson Group Contributions to Ideal-Gas Properties (*Continued*)

GROUP	ΔHf°(298 K) kJ/mol	S°(298 K) J/mol K	Cp°, J/mol K					
			300 K	400 K	500 K	600 K	800 K	1000 K

Nitrogen-containing Compounds

GROUP	ΔHf°(298 K) kJ/mol	S°(298 K) J/mol K	300 K	400 K	500 K	600 K	800 K	1000 K
C-(N)(H)$_3$	-42.20	127.32	25.92	32.82	39.36	45.18	54.51	61.84
C-(N)(C)(H)$_2$	-27.6	41.0	21.98	28.89	34.57	39.31	46.43	51.67
C-(N)(C)$_2$(H)	-21.8	-49.0	19.55	26.46	31.99	35.13	40.03	42.83
C-(N)(C)$_3$	-13.4	-142.8	18.21	25.79	30.61	33.12	35.55	35.59
N-(C)(H)$_3$	20.1	124.4	23.95	27.26	30.65	33.79	39.40	43.84
N-(C)$_2$(H)	64.5	37.4	17.58	21.81	25.67	28.60	33.08	36.22
N-(C)$_3$	102.2	-56.4	14.57	19.09	22.73	25.00	27.47	27.93
N-(N)(H)$_2$	47.7	122.0	25.54	30.90	35.29	38.81	44.13	48.23
N-(N)(C)(H)	87.5	40.2	20.18	24.28	27.21	29.31	32.66	34.75
N-(N)(C)$_2$	122.3	-57.8	6.53	10.47	13.86	16.20	19.34	20.89
N-(N)(C$_B$)(H)	92.5		13.73	16.96	19.89	22.23	26.29	28.93
N$_I$-(H)	(68.2)	(51.5)	12.35	19.18	27.00	32.28	38.23	41.53
N$_I$-(C)	89.2		10.38	13.98	16.54	17.96	19.22	19.26
N$_I$-(C$_B$)	69.9		10.89	13.48	15.95	17.67	20.05	21.44
N$_A$-(H)	105.1	112.2	18.34	20.47	22.78	24.87	28.34	31.07
N$_A$-(C)	136.1	33.5	11.30	17.17	20.60	22.36	23.82	23.91
N-(C$_B$)(H)$_2$	20.1	124.4	23.95	27.26	30.65	33.79	39.40	43.84
N-(C$_B$)(C)(H)	62.4		15.99	20.47	23.91	26.29	30.10	32.36
N-(C$_B$)(C)$_2$	109.7		2.60	8.46	13.69	17.29	21.90	23.40
N-(C$_B$)$_2$(H)	68.2		9.04	13.06	17.29	21.35	28.30	32.99
C$_B$-(N)	-2.1	-40.6	16.54	21.81	24.87	26.46	27.34	27.47
N$_A$-(N)	96.3		8.88	17.50	23.07	28.34	28.72	29.52
CO-(N)(H)	-123.9	146.2	29.43	32.95	36.93	40.53	46.72	51.08
CO-(N)(C)	-137.3	67.8	22.48	25.83	29.60	32.07	40.28	46.85
N-(CO)(H)$_2$	-62.4	103.37	17.04	24.03	29.85	34.71	41.70	46.98
N-(CO)(C)(H)	-18.4	16.3	16.20	21.27	24.91	28.30	28.76	27.38
N-(CO)(C)$_2$	19.7		7.66	15.87	21.94	25.92	29.77	31.07
N-(CO)(C$_B$)(H)	1.7		12.69	16.37	19.26	23.36	26.08	26.46

Cp°, J/mol K

GROUP	ΔHf°(298 K) kJ/mol	S°(298 K) J/mol K	300 K	400 K	500 K	600 K	800 K	1000 K
Nitrogen-containing Compounds (continued)								
N-(CO)₂(H)	-77.5		15.03	23.19	28.05	30.94	33.29	34.29
N-(CO)₂(C)	-24.7		4.48	12.98	18.05	20.93	22.94	27.09
N-(CO)₂(C)	-2.1		4.10	12.81	17.71	20.31	22.11	22.15
C-(CN)(C)(H)₂	94.2	168.31	46.47	56.10	64.90	72.01	82.5	89.18
C-(CN)(C)₂(H)	108.0	82.90	46.05	53.17	59.03	64.48	72.43	77.87
C-(CN)(C)₃	121.4	-11.72	36.22	46.72	53.97	58.82	64.94	67.78
C-(CN)₂(C)₂		-118.91	61.63	74.78	83.74	90.48	99.56	104.50
Cd-(CN)(H)	156.6	153.15	41.03	48.89	55.68	60.71	68.24	72.43
Cd-(CN)(C)	163.91	66.61	40.78	47.23	52.25	55.52	60.50	62.51
Cd-(CN)₂	352.1		56.94	69.29	78.21	84.78	93.53	98.77
Cd-(NO)₂(H)		185.9	51.5	63.2	72.9	80.4	90.4	97.1
CB-(CN)	149.9	85.83	41.0	46.9	51.5	54.9	59.5	62.4
Ct-(CN)	267.1	148.21	43.12	47.31	50.66	53.17	56.94	59.87
C-(NO₂)(C)(H)₂	-63.2	202.6	52.71	66.24	77.54	86.50	99.60	108.44
C-(NO₂)(C)₂(H)	-66.2	112.6	50.20	63.68	74.19	82.10	92.86	99.23
C-(NO₂)(C)₃		16.3	41.41	55.85	66.40	73.77	81.27	87.34
C-(NO₂)₂(C)(H)	-62.4		72.52	95.54	113.34	126.48	143.82	154.20
O-(NO)(C)	-24.7	175.4	38.10	43.12	46.9	50.2	55.7	58.2
O-(NO₂)(C)	-81.2	203.06	39.94	48.32	55.52	65.31	68.62	72.77
Ring Corrections for Nitrogen-containing Compounds								
Ethyleneimine	116.0	132.3	-8.67	-9.13	-9.09	-8.58	-8.12	-7.87
Azetidine	109.7	122.7	-19.80	-18.92	-17.08	-15.11	-11.14	0.04
Pyrrolidine	28.5	118.8	-25.83	-23.36	-20.10	-16.75	-12.02	-9.09
Piperidine	4.2		-2.34	1.55	4.52	6.53	7.16	-1.93
Succinimide	35.6		9.04	17.08	25.71	33.54	38.14	40.91

TABLE 6-4 Benson Group Contributions to Ideal-Gas Properties *(Continued)*

GROUP	ΔH_f^o(298 K) kJ/mol	S^o(298 K) J/mol K	C_p^o, J/mol K					
			300 K	400 K	500 K	600 K	800 K	1000 K
		Halogen Groups						
C-(F)₃(C)	-663.2	177.9	53.2	62.8	68.7	74.9	80.8	83.7
C-(F)₂(H)(C)	-457.6	163.7	41.4	50.2	57.4	63.2	69.9	74.5
C-(F)₂(H)₂(C)	-215.6	148.2	33.9	41.87	50.2	54.43	63.6	69.5
C-(F)₂(C)₂	-406.1	74.5	41.4	49.4	56.5	60.3	67.4	69.5
C-(F)(H)(C)₂	-205.2	58.6	30.56	37.85	43.84	48.40	54.85	58.66
C-(F)(C)₃	-203.1	-	28.47	37.10	42.71	46.72	52.04	53.26
C-(F)₂(Cl)(C)	-445.1	169.6	57.4	67.4	73.3	77.9	82.9	85.4
C-(Cl)₃(C)	-86.7	211.0	68.2	75.4	80.0	82.9	86.2	87.9
C-(Cl)₂(H)(C)	(-79.1)	183.0	50.7	58.6	64.5	69.1	74.9	78.3
C-(Cl)₂(H)₂(C)	-69.1	158.3	37.3	44.8	51.5	56.1	64.1	69.9
C-(Cl)₂(C)₂	-92.1	93.8	51.1	62.30	66.78	69.00	71.01	71.26
C-(Cl)(H)(C)₂	-62.0	73.7	37.7	41.4	44.0	46.9	58.2	61.1
C-(Cl)(C)₃	-53.6	-22.6	38.9	44.0	46.1	47.3	51.9	53.2
C-(Br)₃(C)	-	233.2	69.9	75.4	78.7	81.2	83.3	85.0
C-(Br)(H)₂(C)	-22.6	170.8	38.1	46.1	52.8	57.4	64.9	70.3
C-(Br)(H)(C)₂	-14.2	-	37.39	44.63	50.07	53.76	58.82	61.63
C-(Br)(C)₃	-1.7	-8.4	38.9	46.1	48.1	51.5	55.7	55.7
C-(I)(H)₂(C)	33.5	180.0	38.5	46.1	54.0	58.2	66.2	72.0
C-(I)(H)(C)₂	44.0	89.2	38.5	45.6	51.1	54.4	59.5	62.0
C-(I)(C)(Cd)(H)	55.77	-	34.04	41.95	44.49	52.8	58.6	62.4
C-(I)(Cd)(H)₂	34.29	-	36.93	45.68	54.30	58.78	66.78	72.60
C-(I)(C)₃	54.4	0	41.16	49.19	54.09	56.31	57.74	56.94

GROUP	ΔHf°(298 K) kJ/mol	S°(298 K) J/mol K	Cp°, J/mol K					
			300 K	400 K	500 K	600 K	800 K	1000 K
Halogen Groups (continued)								
C-(Cl)(Br)(H)(C)	—	191.3	51.9	58.6	65.3	68.2	74.9	79.5
N-(F)₂(C)	-32.7	-	34.54	42.41	48.23	53.59	60.16	62.72
C-(Cl)(C)(O)(H)	-90.4	63.	41.24	43.50	46.26	48.44	52.13	55.01
C-(I)₂(C)(H)	(108.9)	(228.6)	53.13	61.88	67.87	71.68	76.66	79.67
C-(I)(O)(H)₂	15.9	170.4	34.42	43.92	51.20	56.73	64.27	69.38
Cd-(F)₂	-324.5	156.2	40.6	46.1	50.2	53.2	57.8	60.7
Cd-(Cl)₂	-7.5	176.3	47.7	52.3	55.7	58.2	61.1	62.8
Cd-(Br)₂	—	199.3	51.5	55.3	58.2	59.9	62.4	63.6
Cd-(F)(Cl)	—	166.6	43.1	49.0	52.8	55.7	59.5	61.5
Cd-(F)(Br)	—	177.9	45.2	50.2	53.6	56.5	59.9	61.5
Cd-(Cl)(Br)	—	188.8	50.7	53.2	56.5	59.0	61.5	61.5
Cd-(F)(H)	-157.4	137.3	28.5	35.2	39.8	44.0	49.4	53.2
Cd-(Cl)(H)	-5.0	148.2	33.1	38.5	43.1	46.9	51.5	54.8
Cd-(Br)(H)	46.1	160.4	33.9	39.8	44.4	47.7	51.9	55.3
Cd-(I)(H)	102.6	169.6	36.8	41.9	45.6	48.6	52.8	55.7
Cd-(C)(Cl)	-8.8	62.8	33.5	35.2	35.6	37.7	38.5	39.4
Cd-(C)(I)	98.8	-	37.3	38.5	38.1	39.4	39.8	40.2
Cd-(Cd)(Cl)	-14.91	-	34.8	38.5	39.4	41.4	41.4	41.4
Cd-(Cd)(I)	92.70	-	38.5	41.4	41.9	43.1	43.1	42.3
Ct-(Cl)	—	139.8	33.1	35.2	36.4	37.7	39.4	40.2
Ct-(Br)	—	151.1	34.8	36.4	37.7	38.5	39.8	40.6
Ct-(I)	—	158.7	35.2	36.8	38.1	38.9	40.2	41.0
CB-(F)	-179.20	67.4	26.4	31.8	35.6	38.1	41.0	42.7
CB-(Cl)	-15.9	79.1	31.0	35.2	38.5	40.6	42.7	43.5
CB-(Br)	44.8	90.4	32.7	36.4	39.4	41.4	43.1	44.0
CB-(I)	100.5	99.2	33.5	37.3	40.2	41.4	43.1	44.0

TABLE 6-4 Benson Group Contributions to Ideal-Gas Properties *(Continued)*

GROUP	ΔH_f^0(298 K) kJ/mol	S^0(298 K) J/mol K	300 K	400 K	500 K	600 K	800 K	1000 K
			— C_p^0, J/mol K					

Halogen Groups (continued)

GROUP	ΔH_f^0(298 K) kJ/mol	S^0(298 K) J/mol K	300 K	400 K	500 K	600 K	800 K	1000 K
C-(C$_B$)(F)$_3$	-681.2	179.2	52.3	64.1	72.0	77.5	84.2	87.9
C-(C$_B$)(Br)(H$_2$)	-28.9		38.90	46.47	52.51	57.32	65.27	69.96
C-(C$_B$)(I)(H)$_2$	35.2		40.95	48.40	54.01	58.95	66.49	70.80
C-(Cl)$_2$(CO)(H)	-74.5		53.6	61.76	66.36	69.71	75.07	77.71
C-(Cl)$_3$(CO)	-82.1		71.2	78.50	81.85	83.53	86.37	87.34
CO-(Cl)(C)	-126.4		37.14	39.52	42.87	46.39	52.46	56.90

Corrections for Next-Nearest-Neighbor Halogen Compounds

GROUP	ΔH_f^0(298 K) kJ/mol	S^0(298 K) J/mol K	300 K	400 K	500 K	600 K	800 K	1000 K
Ortho (F)(F)	20.9		0	0	0	0	0	0
Ortho (Cl)(Cl)	9.2		-2.09	-1.84	-2.30	-2.22	-1.17	-0.08
Ortho (alkane)(halogen)	2.5		1.76	1.84	1.17	0.80	0.50	0.59
Cis (halogen)(halogen)	1.3		-0.75	-0.04	-0.13	-0.71	0	-0.13
Cis (halogen)(alkane)	-3.3		-4.06	-2.93	-2.22	-1.97	-1.00	-0.54

Organosulfur Groups

GROUP	ΔH_f^0(298 K) kJ/mol	S^0(298 K) J/mol K	300 K	400 K	500 K	600 K	800 K	1000 K
C-(H)$_3$(S)	-42.20	127.32	25.92	32.82	39.36	45.18	54.51	61.84
C-(C)(H)$_2$(S)	-23.66	41.37	22.52	29.64	36.01	41.74	51.33	59.24
C-(C)$_2$(H)(S)	-11.05	-47.39	20.31	27.26	32.57	36.38	41.45	44.25
C-(C)$_3$(S)	-2.30	-144.07	19.13	26.25	31.19	34.12	36.51	33.91
C-(C$_B$)(H)$_2$(S)	-19.80		17.21	28.26	36.43	42.50	49.95	54.85
C-(C$_d$)(H)$_2$(S)	-27.00		20.93	29.27	36.30	42.16	51.9	59.83
C$_B$-(S)	-7.5	42.71	16.33	22.19	25.96	27.63	28.89	28.89

C_p^o, J/mol K

Organosulfur Groups (continued)

GROUP	ΔH_f^o(298 K) kJ/mol	S^o(298 K) J/mol K	300 K	400 K	500 K	600 K	800 K	1000 K
Cd-(H)(S)	35.84	33.49	17.42	21.06	24.33	27.21	32.03	35.38
Cd-(C)(S)	45.76	-51.96	14.65	14.95	16.04	17.12	18.46	20.93
S-(C)(H)	19.34	132.03	24.53	25.96	27.26	28.39	30.56	32.28
S-(CB)(H)	50.07	53.00	21.44	22.02	23.32	25.25	29.27	32.82
S-(C)2	48.19	55.06	20.89	20.77	21.02	21.23	22.65	23.99
S-(C)(Cd)	41.74		17.67	21.27	23.28	24.16	24.58	24.58
S-(Cd)2	-19.01	69.00	20.05	23.36	23.15	26.33	33.24	40.74
S-(CB)(C)	80.22		12.64	14.19	15.53	16.91	19.34	20.93
S-(CB)2	108.44		8.37	8.42	9.38	11.47	15.91	19.72
S-(S)(C)	29.52	51.79	21.90	22.69	23.07	23.07	22.52	21.44
S-(S)(CB)	60.7		12.10	14.19	15.57	17.38	20.01	21.35
S-(S)2	12.73	55.94	19.7	20.9	21.4	21.8	22.2	22.6
C-(SO)(H)3	-42.20	127.32	25.92	32.82	39.36	45.18	54.51	61.84
C-(C)(SO)(H)2	-32.32		19.05	26.88	33.29	38.35	48.85	51.16
C-(C)3(SO)	-12.77		12.81	19.18	20.26	27.63	31.57	33.33
C-(Cd)(SO)(H)2	-30.77		18.42	26.63	29.06	38.73	45.93	51.29
CB-(SO)	9.6		11.18	13.15	15.41	17.38	20.77	22.78
SO-(C)2	-60.33	75.78	37.18	41.99	43.96	45.18	45.97	46.77
SO-(CB)2	-50.2		23.95	38.06	40.61	47.94	47.98	47.10
C-(SO2)(H)3	-42.20	127.32	25.92	32.82	39.36	45.18	54.51	61.84
C-(C)(SO2)(H)2	-32.15		22.52	29.64	36.01	41.74	51.33	59.24
C-(C)2(SO2)(H)	-10.97		18.51	26.17	31.65	35.50	40.36	43.12
C-(C)3(SO2)	-2.55		9.71	18.34	23.86	27.17	30.44	31.23
C-(Cd)(SO2)(H)2	-29.89		20.93	29.27	36.30	42.16	51.96	59.83
C-(CB)(SO2)(H)2	-23.19		15.53	27.51	34.57	40.99	49.78	55.27
CB-(SO2)	9.6		11.18	13.15	15.41	17.38	20.77	22.78

TABLE 6-4 Benson Group Contributions to Ideal-Gas Properties *(Continued)*

GROUP	ΔH_f^o(298 K) kJ/mol	S^o(298 K) J/mol K	C_p^o, J/mol K 300 K	400 K	500 K	600 K	800 K	1000 K
			Organosulfur Groups (continued)					
$C_d-(H)(SO_2)$	52.46		12.73	19.55	24.83	28.64	32.95	36.30
$C_d-(C)(SO_2)$	60.58		7.75	13.02	16.66	19.26	22.32	23.74
$SO_2-(C_d)(C_B)$	-287.13		41.41	48.15	55.89	61.17	65.82	66.65
$SO_2-(C_d)_2$	-308.06		48.23	50.12	55.89	59.79	64.39	66.49
$SO_2-(C)_2$	-291.99	87.50	42.62	49.15	54.09	57.65	63.35	66.99
$SO_2-(C)_2(C_B)$	-302.66		41.62	48.15	56.31	60.75	65.40	66.65
$SO_2-(C_B)_2$	-287.13		35.00	46.18	56.73	62.55	66.40	66.82
$SO_2-(SO_2)_2(C_B)$	-319.24		41.07	48.15	56.61	61.67	65.77	67.11
$CO-(S)(C)$	-132.14	64.60	23.40	26.46	29.68	32.49	37.22	40.24
$S-(H)(CO)$	-5.90	130.63	31.95	33.87	34.00	34.21	35.59	34.50
$C-(S)(F)_3$		162.9	41.37	54.47	62.09	68.54	76.07	80.01
$CS-(N)_2$	-132.14	64.60	23.40	26.46	29.68	32.49	37.22	40.24
$N-(CS)(H)_2$	53.51	122.21	25.41	30.48	34.25	37.30	42.24	45.97
$S-(S)(N)$	-20.52		15.5	15.5	15.5	15.5	17.6	17.6
$N-(S)(C)_2$	125.19		16.62	21.65	26.00	29.06	30.94	38.69
$SO-(N)_2$	-132.14		23.40	26.46	29.68	32.49	37.22	40.24
$N-(SO)(C)_2$	66.99		17.58	24.62	25.62	27.34	28.60	34.92
$SO_2-(N)_2$	-132.14		23.40	26.46	29.68	32.49	37.22	40.24
$N-(SO_2)(C)_2$	-85.41		25.20	26.59	31.57	34.46	37.81	38.48
Ring (σ)e,f		Ring Corrections for Sulfur-containing Compounds						
Thiirane (2)	74.11	123.38	-11.93	-10.84	-11.14	-12.64	-18.09	-24.37
Trimethylene sulfide (2)	81.10	113.80	-19.22	-17.50	-16.37	-16.37	-19.26	-23.86
Tetrahydrothiophene(2)	7.24	98.64	-20.52	-19.55	-15.41	-15.32	-18.46	-23.32
Thiacyclohexane (2)	0	73.10	-26.04	-17.84	-9.38	-2.89	3.60	5.40
Thiacycloheptane (2)	16.29		-32.45	-20.60	-5.11	10.84	20.05	19.30
3-Thiocyclopentene {2}	21.23		-26.96	-17.75	-17.71	-17.50	-20.10	-24.95
2-Thiocyclopentene {1}	21.23		-26.96	-17.75	-17.71	-17.50	-10.10	-24.45
Thiophene (2)	7.24	98.64	-20.52	-19.55	-15.41	-15.32	-18.46	-23.32

b. C_d represents a carbon atom that is joined to another carbon atom by a double bond. It is considered divalent. For example, 2-pentene would have the groups $C-(C_d)(H)_3$, $C_d-(C)(H)$ twice, $C-(C_d)(H)_2$, and $C-(C)(H)_3$. C_t represents a carbon atom that is joined to another carbon atom by a triple bond. It is considered monovalent. For example, propyne would have the groups $C_t-(H)$, $C_t-(C)$, and $C-(C_t)(H)_3$. C_B represents a carbon atom in an aromatic ring. It is considered monovalent. For example, p-ethyltoluene would have the groups $C-(C)(H)_3$, $C-(C_B)(H)_2$, $C-(C_B)(H)_3$, $C_B-(C)$ twice, and $C_B-(H)$ four times. C_a represents the allene group, $>C=C=C<$; the end carbons are treated as normal C_d atoms. For example, 1,2-butadiene would have the groups C_a, $C_d-(H)_2$, $C_d-(C)(H)_2$, and $C-(C_d)(H)_3$. C_{BF} represents a carbon atom at the border of two or three fused aromatic rings. For example, benzo[a]pyrene would consist of 12 $[C_B-(H)]$, $4[C_{BF}-(C_B)_2(C_{BF})]$, $2[C_{BF}-(C_B)(C_{BF})_2]$ and $2[C_{BF}-(C_{BF})_3]$.

c. When one of the groups is t-butyl, the cis correction = 16.8; when both are t-butyl, the cis correction = 41.9; and when there are two cis corrections around one double bond, the total correction = 12.6.

d. Value is 5.0 for but-2-ene but zero for other dienes and 2.5 for trienes.

e. The number in parentheses beside each ring is the symmetry number.

f. For $\Delta H_f^0(298\ K)$ contributions for other ring structures, see Chem. Rev. 69, 279 (1969).

g. N_I represents a double-bonded nitrogen in imines; $N_I-(C_B)$ represents a pyridine nitrogen. N_A represents a double-bonded nitrogen in azo compounds. For ortho or para substitution in pyridine add -6.3 kJ/mol per group to $\Delta H_f^0(298\ K)$.

The correction originates in the fact that, from statistical mechanics, the entropy is given by $R \ln W$, where W is the number of distinguishable configurations of a compound. The rotational entropy contributions must be corrected, since by rotating a molecule one often finds indistinguishable configurations and W must be reduced by this factor. If σ is the symmetry number (see below for a more exact definition), the rotational entropy is to be corrected by subtracting $R \ln \sigma$ from the calculated value.

Benson [3] defines σ as "the total number of *independent* permutations of identical atoms (or groups) in a molecule that can be arrived at by simple rigid rotations of the entire molecule." Inversion is not allowed.

It is often convenient to separate σ into two parts, σ_{ext} and σ_{int}, and then

$$\sigma = \sigma_{ext}\sigma_{int} \tag{6-6.1}$$

For example, propane has two terminal $-CH_3$ groups, and each group has a threefold axis of symmetry. Rotation of these *internal* groups yields $\sigma_{int} = (3)(3)$ as the number of permutations. Also, the entire molecule has a single twofold axis of symmetry, so $\sigma_{ext} = 2$. Then $\sigma = (2)(3^2) = 18$. Some additional examples are shown in the accompanying table. Benson et al. [5] show many other examples in their comprehensive review.

	σ_{ext}	σ_{int}	σ
Benzene	(6)(2)	1	12
Methane	4	3	12
p-Cresol	2	3	6
1,3,5-Trimethylbenzene	2	3^4	162
1,2,4-Trimethylbenzene	1	3^3	27
Cyclohexane	6	1	6
Methanol	1	3	3
t-Butyl alcohol	1	3^4	81
Acetone	2	3^2	18
Acetic acid	1	3	3
Aniline	2	1	2
Trimethylamine	3	3^3	81

Corrections for isomers

In addition to the symmetry corrections noted above, if a molecule has optical isomers, i.e., contains one or more completely asymmetric carbon atoms (as in 3-methylhexane), the number of spatial orientations is increased and a correction of $+R \ln \eta$ must be added to the calculated absolute entropy, η being the number of such isomers. The number of possible optical isomers is 2^m, where m is the number of asymmetric carbons. However, in some molecules with more than one asymmetric carbon atom, there exist planes of symmetry which negate the optical activity of some forms. An example is the meso form of tartaric acid.

In a similar manner, Benson [3] indicates that, in molecules of the type ROOH and R−OO−R, the O−H and O−R bonds are at approximately right angles and exist in right- and left-hand forms with a higher entropy by $R \ln 2$.

In summary, when using Benson's method to estimate $S°$ (298 K), one first sums the contributions for the various groups (Δ_S in Table 6-4) and then corrects this sum by

$$S° \text{ (298 K)} = \sum_j n_j \Delta_S - R \ln \sigma + R \ln \eta \tag{6-6.2}$$

where σ is the symmetry number from Eq. (6-6.1) and η is the number of possible optical isomers.

For $\Delta H_f°$ (298 K) and $C_p°$ (T), no symmetry or optical isomer corrections are necessary. For $\Delta H_f°$ (298 K),

$$\Delta H_f° \text{ (298 K)} = \sum_j n_j \Delta_H \tag{6-6.3}$$

and $C_p°$ (T) is obtained by summing the necessary group contributions at the system temperature from Table 6-4.

The method is illustrated in Example 6-4, and estimated values of $C_p°$ (T), $\Delta H_f°$ (298 K), and $S°$ (298 K) are compared with literature values in Tables 6-6 to 6-8. The method is discussed in Sec. 6-8.

Example 6-4   Use Benson's method to estimate $\Delta H_f°$ (298 K), $S°$ (298 K), and $C_p°$ (800 K) for 2-methyl-2-butanethiol. Literature values for these three properties are -127.11 kJ/mol, 387.20 J/(mol·K), and 277.50 J/(mol·K), respectively [25].

solution   2-Methyl-2-butanethiol is composed of the following groups with the contributions from Table 6-4.

Group	Number	Δ_H	Δ_S	$C_p°$ (800 K)
C−(C)(H)$_3$	3	(3)(−42.20)	(3)(127.32)	(3)(54.51)
C−(C)$_2$(H)$_2$	1	−20.72	39.44	46.35
C−(C)$_3$(S)	1	−2.30	−144.07	36.51
S−(C)(H)	1	19.34	137.03	30.56
		−130.88	414.36	276.95

With Eq. (6-6.3),

$\Delta H_f°$ (298 K) $= -130.88$ kJ/mol

Difference $= -130.88 - (-127.11) = -3.8$ kJ/mol

For $S°$ (298 K), the symmetry number of 2-methyl-2-butanethiol is computed with $\sigma_{ext} = 1$, $\sigma_{int} = 3^3$, and, by Eq. (6-6.1), $\sigma = (1)(3^3) = 27$. Then, with Eq. (6-6.2) and $\eta = 1$,

$$S° (298 \text{ K}) = 414.36 - (8.314)(\ln 27) + (8.314)(\ln 1)$$
$$= 386.96 \text{ J/(mol·K)}$$
$$\text{Difference} = 386.96 - 387.20 = -0.3 \text{ J/(mol·K)}$$
$$C_p° (800 \text{ K}) = 276.95 \text{ J/(mol·K)}$$
$$\text{Error} = \frac{276.95 - 277.50}{277.50} \times 100 = -0.2\%$$

6-7 Method of Cardozo [7]

Cardozo has proposed a rather simple method to estimate the enthalpy of combustion and, as shown later, the enthalpy of formation for a wide variety of organic compounds in the gaseous, liquid, and solid states.

The enthalpy of combustion is defined as the difference in enthalpy of a compound and that of its products of combustion in the gaseous state, all at 298 K and 1 atm. The products of combustion are assumed to be $H_2O(g)$, $CO_2(g)$, $SO_2(g)$, $N_2(g)$, and $HX(g)$, where X is a halogen atom. Since product water is in the gaseous state, this enthalpy of combustion would be termed the *lower* enthalpy of combustion.

In the calculations an *equivalent chain length N* is defined as

$$N = N_C + \sum_i \Delta N_i \tag{6-7.1}$$

where N_C is the *total* number of carbon atoms in the compound and ΔN_i are corrections for various structures and phases as shown in Table 6-5. Once N has been determined, the enthalpy of combustion (in kJ/mol) is determined from Eqs. (6-7.2) through (6-7.4).

$$\Delta H_c°(g) = -198.42 - 615.14N \tag{6-7.2}$$
$$\Delta H_c°(l) = -196.98 - 610.13N \tag{6-7.3}$$
$$\Delta H_c°(s) = -206.21 - 606.56N \tag{6-7.4}$$

For the normal alkanes, $N = N_C$. Since the technique applies to quite complex compounds, some examples are shown in Table 6-5 to illustrate its wide applicability.

If one has the enthalpy of combustion, it is possible to obtain an enthalpy of formation by using Eq. (6-7.5),

$$\Delta H_f° (298 \text{ K}) = -393.78N_C - 121.00(N_H - N_X) - 271.81N_F$$
$$- 92.37N_{Cl} - 36.26N_{Br} + 24.81N_I - 297.26N_S - \Delta H_c° \tag{6-7.5}$$

where N_C, N_H, N_F, N_{Cl}, N_{Br}, N_I, and N_S are the numbers of atoms of carbon, hydrogen, fluorine, chlorine, bromine, iodine, and sulfur in the compound and N_X is the total number of halogen atoms. Enthalpies of

formation estimated with Eqs. (6-7.1), (6-7.2), and (6-7.5) are compared with literature values in Table 6-7.

6-8 Discussion and Recommendations

Enthalpy of formation

Six methods were evaluated. Values estimated from these methods are compared with literature values in Table 6-7. The methods of Benson (Sec. 6-6) and Yoneda (Sec. 6-4) yield the smallest errors with only a few large deviations. Both techniques allow for effects of next-nearest neighbors and require some patience to master the method of calculation. Thinh et al.'s procedure (Sec. 6-5) is also quite accurate but is limited to hydrocarbons. These authors [26, 27], in a much wider test, found errors normally less than 1 kJ/mol. Joback's technique is broadly applicable and, on the average, is only slightly less accurate than Benson's or Yoneda's. The large errors encountered for some compounds should, however, be noted.

The procedure suggested by Cardozo (Sec. 6-7) determines the enthalpy of combustion at 298 K, and from this value the enthalpy of formation can be found. The errors in Table 6-7 are comparable to those of Joback's. Cardozo's procedure is, however, most useful for quite complex organic compounds especially when the material is in a condensed phase at the temperature of interest.

It is recommended that, for highest accuracy, the Benson or Yoneda method be selected, but the procedures of Joback and Cardozo also normally provide reliable estimates—and are much simpler to use.

Literature values of ΔH_f° (298 K) are given for many compounds in Appendix A.

Ideal-gas heat capacities

Four estimation methods were presented, and calculated results are compared with literature values in Table 6-6. All techniques are similar in accuracy, and except for quite unusual structures, errors are less than 1 to 2 percent. Joback's method is the easiest to use and has wide applicability. In this case, the coefficients of a third-order polynomial are estimated and used to determine C_p° in an equation form. Yoneda's approach is similar, but only a second-order polynomial is used. Thinh et al.'s equations for heat capacity are more complex and cannot be integrated analytically. Benson tabulates C_p° group values at increments of 100 K.

None of the estimation procedures except the procedure of Thinh et al. should be used outside the approximate range of 280 to 1100 K. The

TABLE 6-5 Cardozo Correction Factors for the Enthalpy of Combustion

A	n-Alkanes	Gas	$\Delta H_c^\circ = -198.42 - 615.14N$
		Liquid	$\Delta H_c^\circ = -196.98 - 610.13N$
		Solid	$\Delta H_c^\circ = -206.21 - 606.56N$

		Per	ΔN_i gas	ΔN_i liquid	ΔN_i solid	Remark
B_1	Carbon-to-carbon branch, alkanes	Branch	For g, l, and s: $-0.031 + 0.012 \ln N_C$			1
B_2	Carbon-to-carbon branch, all other compounds	Branch	-0.02	-0.02	-0.02	
C_1	Cyclopropanes		-0.06	-0.102	—	2
C_2	Cyclobutanes		-0.16	-0.17		2
C_3	Cyclopentanes		-0.277	-0.283	-0.25	2
C_4	Cyclohexanes		-0.311	-0.311	-0.278	2
C_5	Cycloheptanes		-0.29	-0.297		2
C_6	Cyclooctanes and higher		-0.256	-0.269	-0.271	2
D_1	1-Alkenes	Double bond	-0.189	-0.189	-0.189	3
D_2	i-Alkenes (i ≠ 1)	Double bond	-0.205	-0.208	-0.218	3
D_3	Cis		+0.004	+0.003	+0.003	3
D_4	Trans		-0.003	-0.002	-0.002	3
E_1	1-Alkynes	Triple bond	-0.314	-0.342	—	3
E_2	i-Alkynes (i ≠ 1)	Triple bond	-0.34	-0.347	—	3
F_1	Alcohols, primary	-OH	-0.246	-0.297	-0.30	
F_2	Alcohols, secondary	-OH	-0.27	-0.32	-0.33	
F_3	Alcohols, tertiary	-OH	-0.30	-0.36	-0.33	
G	Aldehydes	=O	-0.525	-0.551	-0.52	
H	Ketones	=O	-0.576	-0.609	-0.57	
I	Carboxylic acids	-OOH	-0.94	-1.033	-1.038	
J	Esters	-OO-	-0.857	-0.93	-0.90	
K	Lactones		-1.08	-1.13	-1.19	
L	Ethers	-O-	-0.197	-0.212	-0.25	
M_1	Amines, primary	-NH₂	+0.24	+0.21	+0.18	
M_2	Amines, secondary	=NH	+0.30	+0.27	+0.16	
M_3	Amines, tertiary	≡N-	+0.32	+0.33	+0.14	
N	Amides	-ONH₂	—	-0.542	-0.542	2

Code	Description	Symbol				Ref
O	Lactams				−0.80	2
P	Amino acids				Additional	4
Q	Dipeptides				Σ amino acids, −0.043, +0.44	4
R	Diketopiperazines				Σ amino acids, +0.59	4
S_1	1-Nitro-	$-NO_2$	−0.22	−0.27	—	
S_2	2-Nitro-	$-NO_2$	−0.26	−0.27	−0.28	
S_3	Dinitro-	$=(NO_2)_2$	—	−0.50	−0.50	
S_4	Trinitro-	$\equiv(NO_2)_3$	—	—	−0.64	
T	Nitriles	$\equiv N$	−0.322	−0.36	—	
U	Sulfides	$-S-$	+0.553	+0.535	—	
V	Disulfides	$-S-S-$	+1.049		—	
W	Thiols, primary	$-SH$	+0.546	+0.524	—	
X_1	Fluoro-	$-F$	−0.26	−0.26	—	
X_2	Chloro-	$-Cl$	−0.28	−0.30	−0.30	
X_3	Bromo-	$-Br$	−0.30	−0.33	—	
X_4	Iodo-	$-I$	−0.31	−0.34	−0.34	
Y_1	Benzenes		−1.167	−1.173	−1.173	2
Y_2	Ortho		−0.006	−0.006	−0.006	
Y_3	Meta		−0.002	−0.002	−0.002	
Y_4	Para		−0.001	−0.001	−0.001	
Z	Linear polynuclear aromatic hydrocarbons		—	—	$0.248\text{-}0.236N_c$	5
AA	Quinones		−0.914	−0.95	−0.86	2
BB	Pyridines		—	—	—	6
CC	Anilides		—	—	−0.50	2
DD	Tetrazoles		—	—	+0.12	2
EE	Pyrroles		−0.60	−0.65	−0.69	2
FF	Thiophenes		−0.303	−0.327	—	
GG_1	Monosaccharides	Furanose ring	—	—	−0.52	2
GG_2	Monosaccharides	Pyranose ring	—	—	−0.50	2
HH_1	Di- and oligosaccharides	Furanose ring	—	—	−0.50	2, 7
HH_2	Di- and oligosaccharides	Pyranose ring	—	—	−0.47	2, 7

TABLE 6-5 Cardozo Correction Factors for the Enthalpy of Combustion (Continued)

Examples of the Cardozo Method to Estimate the Enthalpy of Combustion

Compound	Structure	Physical state	Calculation of N		ΔH_c° (kJ/mol) Lit.	Calc.
Vinyl chloride	$CH_2=CHCl$	Gas	$(2 + D_1) + X_2$	= 1.531	-1157	-1140
Ethane	CH_3CH_3	Gas	(2)	= 2	-1429	-1429
Acrolein	$CH_2=CHCHO$	Liquid	$(3 + D_1) + G$	= 2.260	-1560	-1576
Asparagine	$H_2NCOCH_2CH(NH_2)COOH$	Solid	$(4) + I + M_1 + N + P$	= 2.557	-1754	-1757
Succinamide	$H_2NCOCH_2-CH_2CONH_2$	Solid	$(4) + 2 \times N$	= 2.916	-1962	-1975
Crotononitrile	$CH_3CH=CHCN$	Liquid	$(4 + D_2 + D_4) + T$	= 3.430	-2286	-2290
Vinylacetylene	$CH_2=CH-C\equiv CH$	Gas	$(4 + D_1 + E_1)$	= 3.497	-2364	-2350
L-Gulonic acid- γ-lactone	$CH_2OH-CHOH-CH-CHOH-CHOH-CO$ ⌐O	Solid	$(6 + K) + F_1 + 3 \times F_2$	= 3.52	-2352	-2341
2,4-Dinitrophenol	$C_6H_3(OH)(NO_2)_2$	Solid	$(6 + Y_1 + Y_2 + Y_4) + F_2 + S_3$	= 3.990	-2614	-2626
Methyl propyl sulfide	$CH_3-S-C_3H_7$	Gas	$(4) + U$	= 4.553	-3000	-2999
Phthalic acid	$C_6H_4(COOH)_2$	Solid	$(8 + 2 \times B_2 + Y_1 + Y_2) + 2 \times I$	= 4.705	-3093	-3060
Isopentylamine	$CH_3CH(CH_3)CH_2CH_2NH_2$	Liquid	$(5 + B_2) + M_1$	= 5.19	-3346	-3364
Anisole	$C_6H_5-O-CH_3$	Liquid	$(7 + Y_1) + L$	= 5.615	-3613	-3623
5-Phenylaminotetrazole	$(CN_4H)-NH-C_6H_5$	Solid	$(7 + Y_1 + DD) + M_2$	= 6.107	-3909	-3910
2,4-Dimethyl-3-pentanone	$CH_3CH(CH_3)COCH(CH_3)CH_3$	Liquid	$(7 + 2 \times B_2) + H$	= 6.351	-4070	-4072
2,2,3-Trimethylbutane	$CH_3C(CH_3)_2CH(CH_3)CH_3$	Liquid	$(7 + 3 \times B_1)$	= 6.977	-4455	-4454
α-Naphthol	$C_{10}H_7OH$	Solid	$(10 + Z) + F_2$	= 7.558	-4787	-4791
1,2,4-Trimethylbenzene	$C_6H_3(CH_3)_3$	Gas	$(9 + 3 \times B_2 + Y_1 + Y_2 + Y_4)$	= 7.766	-4982	-4976
Eugenol	$C_6H_3(OH)(OCH_3)(CH_2-CH=CH_2)$	Liquid	$(10 + B_2 + D_1 + Y_1 + HH_1 + HH_2) + 3 \times F_1 + F_2 + L$	= 8.079	-5123	-5126
Sucrose	$[CH(CH_2OH)-CHOH-CHOH-CHOH-CH] \diagdown O$ $[(CH_2OH)CH-CHOH-CHOH-C(CH_2OH)] \diagup O$	Solid	$(12 + 3 \times B_2 + HH_1 + HH_2) + 3 \times F_1 + 5 \times F_2 + L$	= 8.17	-5160	-5162
2,2'-Difluorobiphenyl	$FC_6H_4-C_6H_4F$	Gas	$(12 + 2 \times B_2 + 2 \times Y_1) + 2 \times X_1$	= 9.106	-5794	-5800
Ethyl 4-ethyl-3,5-dimethyl-pyrrole-2-carboxylate	$(C_4HN)(C_2H_5)(CH_3)_2(CO_2C_2H_5)$	Solid	$(11 + 4 \times B_2 + EE) + J$	= 9.33	-5865	-5865
Benzanilide	$C_6H_5-NH-CO-C_6H_5$	Solid	$(13 + B_2 + 2 \times Y_1) + CC$	= 10.134	-6357	-6353
Diphenylacetylene	$C_6H_5C\equiv CC_6H_5$	Solid	$(14 + 2 \times B_2 + E_2 + 2 \times Y_1)$	= 11.267	-7043	-7040

Compound	Formula	State	Equation	Calc.		
Valylphenylalanine	$(C_6H_5)CH_2CH(NH)COOH$ $CH_3CH(CH_3)CH(NH_2)CO$	Solid	Valine : $(5 + B_2) + I + M_1 + P$ Phen.al.: $(9 + B_2 + Y_1) + I + M_1 + P$ Dipept.: $+Q$	$= 4.079$ $= 6.906$ $\underline{0.44\ +}$ $= 11.425$	-7164	-7136
Dicyclohexylmethane	$(C_6H_{11})_2CH_2$	Liquid	$(13 + 2 \times B_2 + 2 \times C)$	$= 12.38$	-7724	-7750
Pentacene-6,13-quinone	$C_{22}H_{12}O_2$	Solid	$(22 + Z) + AA$	$= 16.202$	-10041	-10034
5-Butyldocosane	$CH_3(CH_2)_3 - CH(C_4H_9) - (CH_2)_{16}CH_3$	Liquid	$(26 + B_1)$	$= 25.997$	-16056	-16059
Dotriacontane	$CH_3(CH_2)_{30}CH_3$	Solid	(32)	$= 32.0$	-19616	-19616
Glyceroltribrassidate	$CH_2(OCOR)CH(OCOR)CH_2(OCOR)$ with R = $CH_3(CH_2)_7CH = CH(CH_2)_{10}CH_2$-(trans)	Solid	$(69 + 3 \times D_2 + 3 \times D_4) + 3 \times J$	$= 65.640$	-40041	-40021

Remarks

1. The correction factor for branched alkanes has an upper limit of -0.003.

2. The carbon atoms forming the ring in cyclic compounds count in the determination of N_C. Functional groups, connected to a carbon atom that is part of a ring and that is connected to two other carbon atoms, are considered as secondary groups. Furthermore, for a carbon atom branched to a carbon atom that is part of a ring, a branch correction should be applied.

3. The correction factors are of general nature and can be used for all compounds with multiple bonds. The cis/trans corrections are valid for all compounds having such structural isomers.

4. The correction for amino acids is calculated by the normal procedure with the addition of the group corrections for amine and carboxylic acid plus an additional constant equal to -0.043. For the amino acid derivatives, the correction consists of the correction factors of the basic amino acids plus an additional structural correction.

5. The correction for linear polynuclear hydrocarbons is calculated for the number of carbon atoms that form the basic structure. It is observed that nonlinear polynuclear hydrocarbons like phenanthrene and chrysene fit well, but for condensed polynuclear hydrocarbons like pyrene and fluoranthrene, the calculated enthalpy of combustion may be up to 2 percent too high.

6. For anilides, the correction factor given is valid for the structural components (NH $-$ and $=$O). For the rest of the molecule, the normal rules apply.

7. The oxygen bridge is considered as an ether bond. For the rest, the normal procedures apply.

TABLE 6-6 Comparison of Estimated and Literature Values for the Ideal-Gas Heat Capacity

Compound	T, K	C_p^o J/mol K [25]	Per Cent Error[a] Calculated by the Method of:			
			Joback Table 6-1	Benson Table 6-4	Yoneda Table 6-2	Thinh et al. Table 6-3
Propane	298	73.94	1.1	0.9	0.6	-0.5
	800	155.25	-0.4	0.6	0.5	0.2
n-Heptane	298	166.09	-0.2	0.4	0.1	-0.1
	800	340.93	-0.2	0.6	0.3	0.8
2,2,3-Trimethylbutane	298	164.67	0.9	0.8	0.3	0.7
	800	346.37	0.1	0.7	0.5	1.0
trans-2-Butene	298	87.88	-4.6	-1.8	1.0	0
	800	173.75	-0.3	-0.1	0.6	0.1
3,3-Dimethyl-1-butene	298	126.57	4.7	4.6	4.5	6.6
	800	266.28	2.5	3.5	2.6	4.3
2-Methyl-1,3-butadiene	298	104.7	-4.4	0.7	1.7	-2.0
	800	201.0	-2.2	0.5	1.0	-1.2
2-Pentyne	298	98.77	2.0	-0.2	1.1	-0.3
	800	192.17	0.7	0.8	0.6	0.4
p-Ethyltoluene	298	151.65	0.9	0.8	0.4	-1.3
	800	324.90	0.3	0.5	0.5	-0.5
2-Methylnaphthalene	298	159.89	-2.3	0	0.6	-2.2
	800	343.44	-1.6	0.9	0.6	-0.4
cis-1,3-Dimethylcyclopentane	298	134.56	1.3	-5.9	0.4	0
	800	317.53	3.5	-1.1	0.5	0.1
2-Butanol	298	113.38	-1.9	-0.8	-2.1	
	800	220.56	-0.1	0.5	0.2	
p-Cresol	298	124.56	0.9	0.1	1.9	
	800	255.86	0.1	-0.1	3.9	
Isopropyl ether	298	158.39	0	-0.8	1.9	
	800	311.46	1.3	2.3	1.3	
p-Dioxane	298	94.12	-0.4	-1.0	-	
	800	218.34	0.1	0	-	
Methyl ethyl ketone	298	102.95	-5.1	-2.5	-4.1	
	800	192.93	0.6	-0.1	-0.3	

Compound	T, K	C_p^o J/mol K [25]	Per Cent Error[a] Calculated by the Method of:			
			Joback Table 6-1	Benson Table 6-4	Yoneda Table 6-2	Thinh et al. Table 6-3
Ethyl acetate	298	113.71	-0.4	-0.5	-28.	
	800	213.57	0.2	0.1	-11.	
Trimethyl amine	298	91.82	-0.2	0.3	0.2	
	800	191.00	0.1	0.5	0.4	
Propionitrile	298	73.10	1.9	-1.4	1.1	
	800	134.56	0.8	2.1	1.7	
2-Nitrobutane	298	123.55	2.0	1.0	1.4	
	800	248.86	-0.3	0.1	0.3	
3-Picoline	298	99.65	2.2	-	-	
	800	222.40	-0.4	-	-	
1,1-Difluoroethane	298	67.99	-0.5	-1.3	4.1	
	800	124.31	0.3	0.6	0.9	
Octafluorocyclobutane	298	156.25	-12.	-6.8	-	
	800	245.56	-1.5	5.5	-	
Bromobenzene	298	97.76	-0.1	2.8	1.7	
	800	200.05	0	1.1	4.6	
Trichloroethylene	298	80.26	1.4	0.3	-5.1	
	800	112.79	-2.8	0.1	-2.9	
Butyl methyl sulfide	298	140.84	0.2	-0.1	0.3	
	800	278.55	-2.1	-0.1	-0.5	
2-Methyl-2-butanethiol	298	146.31	-1.5	0.4	-0.9	
	800	277.50	-0.1	-0.2	0.2	
Propyl disulfide	298	185.48	-0.2	0.4	1.2	
	800	350.44	-1.8	0.4	-1.3	
3-Methylthiophene	298	94.91	1.8	0.3	-	
	800	192.38	1.0	2.5	-	
Number of Compounds			28	27	24	10
Average Absolute Error, Per Cent			1.4	1.1	1.4b	1.1

a. $[(calc.-lit.)/lit.]\times100$;
b. Values do not include the large anomalous errors for ethyl acetate

TABLE 6-7 Comparison between Estimated and Literature Values for the Enthalpy of Formation at 298 K

Compound	ΔH_f° kJ/mol [25]	Difference[a], kJ/mole, as Calculated by the Method of:				
		Joback Table 6-1	Benson Table 6-4	Yoneda Table 6-2	Thinh et al. Table 6-3	Cardozo Table 6-5
Propane	-103.92	-1.4	-1.2	-1.9	0	-1.5
n-Heptane	-187.90	0.1	-0.1	0.3	0.1	-0.1
2,2,3-Trimethylbutane	-204.94	3.0	1.5	2.6	-0.1	2.8
trans-2-Butene	-11.18	2.5	-1.3	-0.8	0	-0.8
3,3-Dimethyl-1-butene	-43.17	-7.4	-14.	-12.	-25.	-23.
2-Methyl-1,3-butadiene	75.78	19.	0	-0.9	4.8	6.8
2-Pentyne	128.95	-1.5	-2.5	-1.6	-5.0	-0.8
p-Ethyltoluene	-3.27	-1.9	-0.1	2.3	0.6	-1.1
2-Methylnaphthalene	116.18	30.	2.9	0	-0.9	-4.2
cis-1,3-Dimethylcyclopentane	-135.95	15.	-0.2	0	0	-17.
2-Butanol	-292.49	9.4	-1.5	-1.8		0.3
p-Cresol	-125.48	-3.1	-0.8	-2.3		8.6
Isopropyl ether	-319.03	9.0	-2.1	-4.9		5.9
p-Dioxane	315.27	0	8.0	-		-
Methyl ethyl ketone	-238.52	0	0.8	-0.5		0.1
Ethyl acetate	-443.21	0	9.5	-1.1		32.
Methyl methacrylate	-332.0	16.	-9.3	-20.		14.
Trimethyl amine	-23.86	-14.	-0.6	0		-5.8
Propionitrile	50.66	9.0	1.3	3.3		8.8
2-Nitrobutane	-163.7	22.	-7.5	3.3		-1.3

Compound	ΔH_f^0 kJ/mol [25]	Difference[a], kJ/mole, as Calculated by the Method of:				
		Joback Table 6-1	Benson Table 6-4	Yoneda Table 6-2	Thinh et al. Table 6-3	Cardozo (Table 6-5)
3-Picoline	106.22	-4.0	-	-	-	-1.1
1,1-Difluoroethane	-494.	13.	-4.	11.	-	30.
Octafluorocyclobutane	-1529.	-	14.	-	-	-
Bromobenzene	105.1	-9.3	8.8	0	-	-1.2
Trichloroethylene	-5.86	-19.	7.1	-22.	-	-
Butyl methyl sulfide	-102.24	-2.4	0.9	0.7	-	-1.6
2-Methyl-2-butanethiol	-127.11	10.	-3.2	2.4	-	6.7
Propyl disulfide	-117.27	34.	3.1	2.1	-	0.7
3-Methylthiophene	82.86	0.8	0.4	-	-	0.4

a. Difference = (Calculated - Literature), kJ/mol

TABLE 6-8 Comparison between Estimated and Literature Values of the Entropy at 298 K

Compound	S°(298 K) J/mol K [25]	Difference[a], J/mol K, as Calculated by the Method of:		
		Benson Table 6-4	Yoneda Table 6-2	Thinh et al. Table 6-3
Propane	270.09	0	3.3	0
n-Heptane	428.18	-0.4	1.0	-1.0
2,2,3-Trimethylbutane	383.55	0.8	1.5	-12.
trans-2-Butene	296.68	0.7	4.2	0
3,3-Dimethyl-1-butene	343.99	5.0	7.6	-13.
2-Methyl-1,3-butadiene	315.85	-0.9	1.5	2.6
2-Pentyne	332.01	0.7	-4.8	6.3
p-Ethyltoluene	399.17	-0.9	-0.3	-7.5
2-Methylnaphthalene	380.29	5.1	0	8.2
cis-1,3-Dimethylcyclopentane	367.06	0.9	0	0
2-Butanol	359.27	2.1	-7.3	
p-Cresol	347.88	4.6	4.4	
Isopropyl ether	390.50	21.	0.9	
Methyl ethyl ketone	338.34	1.1	-3.4	
Ethyl acetate	363.00	13.	1.2	
Trimethyl amine	288.97	0.1	0	
Propionitrile	286.80	-0.4	-4.4	
2-Nitrobutane	383.59	11.	2.0	
1,1-Difluoroethane	282.69	-0.9	-8.3	
Octafluorocyclobutane	400.63	4.9	-	
Bromobenzene	324.60	1.4	0	
Trichloroethylene	325.02	-0.5	17.	
Butyl methyl sulfide	412.11	-0.4	-0.8	
2-Methyl-2-butanethiol	387.20	-0.3	-0.8	
Propyl disulfide	495.30	0.5	-2.7	
3-Methylthiophene	321.50	-3.1	-	

a. Difference = Calculated - Literature, J/mol K

Thinh et al. form has been demonstrated (for hydrocarbons) to extend from about 200 to 1500 K. Appendix A presents specific polynomial constants for many compounds. Values given in this data bank should be used in preference to those estimated by methods in this chapter.

Other authors have tabulated polynomial constants for C_p° [20, 21], and new equations to express C_p° as a function of temperature have been suggested [1, 11, 13, 28].

Entropies

Three procedures were evaluated to estimate the absolute entropy of 298 K. Calculated results are compared with literature values in Table 6-8. All three have about the same degree of accuracy, but Thinh et al.'s is limited to hydrocarbons. A disadvantage of Benson's method is the necessity of determining the symmetry number of the compound, a task often requiring the construction of three-dimensional models to determine the symmetry planes. Neither Yoneda's nor Thinh et al.'s procedure requires such a correction.

Gibbs energy of formation

Two techniques were tested, Joback's and Thinh et al.'s. The latter is significantly more accurate, although it is limited to hydrocarbons. For non-hydrocarbons we recommend the method of Joback, although it may lead to relatively large errors for complex materials. No symmetry or optical isomer corrections are necessary. Estimated values are compared with those reported in the literature in Table 6-9. Generally, Joback's method is within 5 to 10 kJ/mol of the literature value. An interesting suggestion was made by Fredenslund and Rasmussen [12] to estimate ΔG_f° from UNIFAC group contributions.

Some literature values of ΔG_f° (298 K) are tabulated in Appendix A.

Notation

C_p°	ideal-gas heat capacity at constant pressure, J/(mol·K)
ΔG_f°	standard Gibbs energy of formation at T and 1 atm, kJ/mol; ΔG° (T), standard Gibbs energy change in a reaction at T
ΔH_c°	standard (lower) enthalpy of combustion at 298 K, kJ/mol
ΔH_f°	standard enthalpy of formation at T, kJ/mol; ΔH° (T), standard enthalpy of reaction at T
n_j	number of groups of type j
N	equivalent chain length; ΔN_i, corrections for the equivalent chain length, Table 6-5; N_C, number of carbon atoms in a compound; simi-

TABLE 6-9 Comparison between Estimated and Literature Gibbs Energy of Formation at 298 K (Reference state is 1 atmosphere.)

Compound	$\Delta G_f^o(298 \text{ K})$ kJ/mol [25]	Difference[a], kJ/mol, as Calculated by the Method of:	
		Joback Table 6-1	Thinh et al. Table 6-3
Propane	-23.49	-2.2	0
n-Heptane	8.00	0	0.4
3-Methylhexane	4.61	0.9	-0.4
2,4-Dimethylpentane	3.10	0	-5.2
2,2,3-Trimethylbutane	4.27	4.1	-7.5
Cyclopentane	38.64	-3.2	0
Cyclohexane	31.78	0	0
Methylcyclopentane	35.80	0.4	0
Ethylene	68.16	-6.7	0
1-Butene	71.34	-0.7	-4.0
cis-2-Butene	65.90	-2.9	0
trans-2-Butene	63.01	0	0
1,3-Butadiene	150.77	7.7	0
Acetylene	209.34	0	0
Methylacetylene	194.56	2.9	-0.6
Benzene	129.75	-8.0	0
Ethylbenzene	130.67	-1.8	0
o-Xylene	122.17	-2.9	-7.2
m-Xylene	118.95	0.3	-4.0
Ethyl mercaptan	-4.69	0	
Dimethyl sulfide	17.79	-1.9	
Thiophene	126.86	0	
Aniline	166.80	12.	
Ethyl amine	37.30	-4.9	
Pyridine	190.33	0	
Dimethyl ether	-113.00	-26.	
Acetaldehyde	-133.39	-0.2	
Acetone	-153.15	-1.4	
Methyl formate	-297.39	0	
Acetic acid	-376.94	-1.0	
Ethyl acetate	-327.62	0	
n-Propyl alcohol	-163.08	-0.6	
Isopropyl alcohol	-173.71	8.5	
Phenol	-32.91	0	
Phosgene	-206.91	12.	
Methyl chloride	-62.93	8.5	
Methylene chloride	-68.91	2.6	
Chloroform	-68.58	-12.	
Carbon tetrachloride	-58.28	-29.	
Ethyl bromide	-26.33	6.6	
Dichlorodifluoromethane	-394.8	-11.	
Fluorobenzene	-69.08	-14.	
Chlorobenzene	99.23	1.0	

a. Difference = Calculated - Literature, kJ/mol

larly for N_F, N_{Cl}, N_{Br}, N_I, N_S, N_X for fluorine, chlorine, bromine, iodine, sulfur, and halogen atoms

R gas constant, 8.314 J/(mol·K)

$S°$ absolute entropy at T, 1 atm, J/(mol·K); $\Delta S°$ (T), standard entropy change of reaction at T; $\Delta S_f°$, standard entropy of formation at T, 1 atm

T temperature, K; T_b, normal boiling temperature at 1 atm

W number of distinguishable configurations of a molecule

GREEK

η number of optical isomers

ν_j stoichiometric multiplier, positive for products, negative for reactants

σ symmetry number; σ_{ext}, for rigid body rotation; σ_{int}, for rotation of subgroups constituting the molecule

Δ_H group contribution for $\Delta H_f°$; Δ_S, for $S°$; Δ_G, $\Delta G_f°$; Δ_a, Δ_b, Δ_c, Δ_d for polynomial coefficients in $C_p°$ equations

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Vapor Pressures
and Enthalpies
of Vaporization
# of Pure Fluids

7-1 Scope

This chapter covers methods for estimating and correlating vapor pressures of pure liquids. Since enthalpies of vaporization are often derived from vapor pressure–temperature data, the estimation of this property also is included.

7-2 Theory and Corresponding States
Correlations

When the vapor phase of a pure fluid is in equilibrium with the liquid phase, the equality of chemical potential, temperature, and pressure in both phases leads to the Clausius-Clapeyron equation

$$\frac{dP_{vp}}{dT} = \frac{\Delta H_v}{T \, \Delta V_v} = \frac{\Delta H_v}{(RT^2/P_{vp}) \, \Delta Z_v} \tag{7-2.1}$$

$$\frac{d \ln P_{vp}}{d(1/T)} = -\frac{\Delta H_v}{R \, \Delta Z_v} \tag{7-2.2}$$

In this equation, ΔH_v and ΔZ_v refer to differences in the enthalpies and compressibility factors of saturated vapor and saturated liquid.

Most vapor pressure estimation and correlation equations stem from an integration of Eq. (7-2.2). When this is done, an assumption must be made regarding the dependence of the group $\Delta H_v/\Delta Z_v$ on temperature. Also, a constant of integration which must be evaluated by using one vapor pressure–temperature point is obtained.

The simplest approach is to assume that the group $\Delta H_v/R\,\Delta Z_v$ is constant and independent of temperature. Then, with the constant of integration denoted as A, Eq. (7-2.2) becomes

$$\ln P_{\mathrm{vp}} = A - \frac{B}{T} \tag{7-2.3}$$

where $B = \Delta H_v/R\,\Delta Z_v$. Equation (7-2.3) is sometimes called the Clapeyron equation. Surprisingly, it is a fairly good relation for approximating vapor pressure over small temperature intervals. Except near the critical point, both ΔH_v and ΔZ_v are weak functions of temperature, and since both decrease with rising temperature, the result is a compensatory effect. However, over large temperature ranges, Eq. (7-2.3) normally represents vapor pressure data poorly. This is shown in Fig. 7-1. The ordinate is the ratio $(P_{\mathrm{exp}} - P_{\mathrm{calc}})/P_{\mathrm{exp}}$, and the abscissa $T_r = T/T_c$. P_{calc} is obtained from Eq. (7-2.3), where the constants A and B are found from experimental data at $T_r = 0.7$ and 1.0. At high reduced temperatures, the fit is reasonably good for oxygen and a typical hydrocarbon, 2,2,4-trimethylpentane, but poor for an associating liquid, n-butanol. Ambrose [2] points out the complexity of the curves in this figure and notes that, to represent the changes in curvature that are evident, at least a four-constant vapor pressure equation would be necessary. Also, it is important to note that there is usually a change in curvature at a T_r between 0.8 and 0.85; this fact is utilized in several later developments.

Extending our consideration of Eq. (7-2.3) one step further, a common practice is to use both the normal boiling point and the critical point to obtain generalized constants. Expressing pressures in bars and temperatures on the absolute scale (kelvins or degrees Rankine), with $P = P_c$, $T = T_c$, and $P = 1.01325$, $T = T_b =$ boiling temperature at 1 atm $= 1.01325$ bar, Eq. (7-2.3) becomes

$$\ln P_{\mathrm{vp}r} = h\left(1 - \frac{1}{T_r}\right) \tag{7-2.4}$$

$$h = T_{br}\,\frac{\ln (P_c/1.01325)}{1 - T_{br}} \tag{7-2.5}$$

Figure 7-1 shows that the linear form of $\ln P_{\mathrm{vp}}$ versus $1/T$ is not satisfactory for associating materials. Equation (7-2.3) generally overpredicts vapor pressures below T_b (see Fig. 7-1 or Table 7-2).
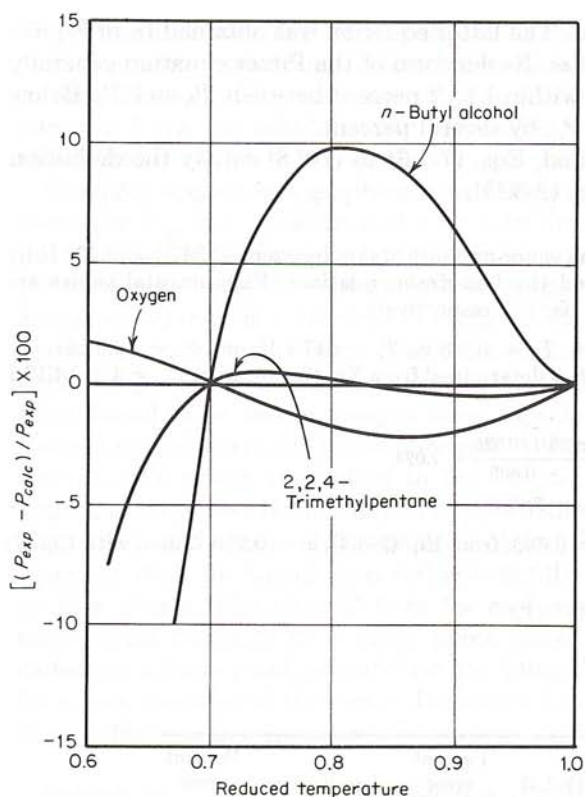
Figure 7-1 Comparison of the simple Clapeyron equation with experimental vapor pressure data. (Adapted from Ref. 2.)

Equation (7-2.4) is a two-parameter corresponding states equation for vapor pressure. To achieve more accuracy, several investigators have proposed three-parameter forms. The Pitzer expansion is one of the more successful:

$$\ln P_{\mathrm{vp}_r} = f^{(0)}(T_r) + \omega f^{(1)}(T_r) \qquad (7\text{-}2.6)$$

The functions $f^{(0)}$ and $f^{(1)}$ have been expressed in tabular form by several authors [18, 70]; they have been expressed in analytical form by Lee and Kesler [56]:

$$f^{(0)} = 5.92714 - \frac{6.09648}{T_r} - 1.28862 \ln T_r + 0.169347 T_r^6 \qquad (7\text{-}2.7)$$

$$f^{(1)} = 15.2518 - \frac{15.6875}{T_r} - 13.4721 \ln T_r + 0.43577 T_r^6 \qquad (7\text{-}2.8)$$

Values of the acentric factor ω are tabulated in Appendix A for many fluids; but when Eq. (7-2.6) is employed, it is recommended that Eq. (2-

3.4) be used to compute ω. The latter equation was obtained from Eq. (7-2.6) with $T_r = T_{br}$. The Lee-Kesler form of the Pitzer equation generally predicts vapor pressures within 1 to 2 percent between T_b and T_c. Below T_b, it may underpredict P_{vp} by several percent.

As can readily be verified, Eqs. (7-2.6) to (7-2.8) satisfy the definition of the acentric factor [Eq. (2-3.1)].

Example 7-1   Estimate the vapor pressure of ethylbenzene at 347.2 and 460 K by using both Eq. (7-2.4) and the Lee-Kesler relations. Experimental values are 0.133 bar [101] and 3.325 bar [3], respectively.

solution   From Appendix A, $T_b = 409.3$ K, $T_c = 617.1$ K, and $P_c = 36.0$ bar. EQUATION (7-2.4).   First h is determined from Eq. (7-2.5), with $T_{br} = 409.3/617.1 = 0.663$,

$$h = 0.663 \frac{\ln 36/1.01325}{1 - 0.663} = 7.024$$

Then $\ln P_{vpr} = 7.024(1 - T_r^{-1})$

LEE-KESLER   With $T_{br} = 0.663$, from Eq. (2-3.4), $\omega = 0.299$. Then, with Eq. (7-2.6),

$$\ln P_{vpr} = f^{(0)}(T_r) + 0.299 f^{(1)}(T_r)$$

For the cases considered,

Vapor Pressure, bar

T, K	T_r	Exp.	Eq. (7-2.4)	Percent error	Lee-Kesler	Percent error
347.2	0.563	0.133	0.155	16	0.132	−0.8
460	0.745	3.325	3.252	−2.2	3.353	0.8

The error was calculated as [(calc. − exp.)/exp.] × 100.

7-3 Antoine Vapor Pressure Correlation

Antoine [10] proposed a simple modification of Eq. (7-2.3) which has been widely used over limited temperature ranges.

$$\ln P_{vp} = A - \frac{B}{T + C} \tag{7-3.1}$$

When $C = 0$, Eq. (7-3.1) reverts to the Clapeyron equation (7-2.3).

Simple rules have been proposed [30, 89] to relate C to the normal boiling point for certain classes of materials; but these rules are not reliable, and the only way to obtain values of the constants is to regress experimental data [15, 46, 58, 63, 74, 88].

Values of A, B, and C are tabulated for a number of materials in Appendix A with P_{vp} in bars and T in kelvins. The applicable temperature range is not large and in most instances corresponds to a pressure interval of

about 0.01 to 2 bar. The Antoine equation should never be used outside the stated temperature limits. Extrapolation beyond these limits may lead to absurd results. The constants A, B, and C form a set. Never use one constant from one tabulation and the other constants from a different tabulation.

Cox [23] suggested a graphical correlation in which the ordinate, representing P_{vp}, is a log scale, and a straight line (with a positive slope) is drawn. The sloping line is taken to represent the vapor pressure of water (or some other reference substance). Since the vapor pressure of water is accurately known as a function of temperature, the abscissa scale can be marked in temperature units. When the vapor pressure and temperature scales are prepared in this way, vapor pressures for other compounds are often found to be nearly straight lines, especially for homologous series. Calingaert and Davis [17] have shown that the temperature scale on this Cox chart is nearly equivalent to the function $(T + C)^{-1}$, where C is approximately -43 K for many materials boiling between 273 and 373 K. Thus the Cox chart closely resembles a plot of the Antoine vapor pressure equation. Also, for homologous series, a useful phenomenon is often noted on Cox charts. The straight lines for each member of the homologous series often converge to a single point when extrapolated. This point, called the infinite point, is useful for providing one value of vapor pressure for a new member of the series. Dreisbach [25] presents a tabulation of these infinite points for several homologous series.

Example 7-2 Calculate the vapor pressure of acrylonitrile at 293.15 K by using the Antoine equation.

solution From Appendix A, $A = 9.3051$, $B = 2782.21$, and $C = -51.15$. With Eq. (7-3.1),

$$\ln P_{vp} = 9.3051 - \frac{2782.21}{293.15 - 51.15}$$

$$P_{vp} = 0.112 \text{ bar}$$

The literature value is 0.117 bar [15] and

$$\text{Error} = \frac{0.112 - 0.117}{0.117} \times 100 = -4.3\%$$

Usually, in the range 0.01 to 2 bar, the Antoine equation provides an excellent correlating equation for vapor pressures. When Antoine parameters are determined from data in this pressure range (as they usually are), the equation underpredicts vapor pressures at higher pressures.

7-4 Gomez-Thodos Vapor Pressure Equation

Gomez-Nieto and Thodos [34 to 36] have presented the following equation for estimating vapor pressures:

$$\ln P_{vpr} = \beta \left[\frac{1}{T_r^m} - 1 \right] + \gamma [T_r^7 - 1] \tag{7-4.1}$$

Equation (7-4.1) is necessarily satisfied at the critical point. The normal boiling point provides an additional equation which relates the constants β, γ, and m to each other. This leads to

$$\gamma = ah + b\beta \tag{7-4.2}$$

where $a = \dfrac{1 - 1/T_{br}}{T_{br}^7 - 1} \tag{7-4.3}$

and $b = \dfrac{1 - 1/T_{br}^m}{T_{br}^7 - 1} \tag{7-4.4}$

h is given by Eq. (7-2.5). Compounds are divided into three classes: nonpolar, polar, and hydrogen-bonded compounds. The procedure for determining m, β, and γ is different for each class. For nonpolar compounds (both organic and inorganic) [34]

$$\beta = -4.26700 - \frac{221.79}{h^{2.5} \exp 0.0384h^{2.5}} + \frac{3.8126}{\exp (2272.44/h^3)} + \Delta^* \tag{7-4.5}$$

$$m = 0.78425 \exp (0.089315h) - \frac{8.5217}{\exp (0.74826h)} \tag{7-4.6}$$

where $\Delta^* = 0$ except for He ($\Delta^* = 0.41815$), H_2 ($\Delta^* = 0.19904$) and Ne ($\Delta^* = 0.02319$). γ is obtained from Eq. (7-4.2).

For polar compounds except water and alcohols [35],

$$m = 0.466 T_c^{0.166} \tag{7-4.7}$$

$$\gamma = 0.08594 \exp (7.462 \times 10^{-4} \, T_c) \tag{7-4.8}$$

For water and alcohols [35]

$$m = 0.0052 M^{0.29} T_c^{0.72} \tag{7-4.9}$$

$$\gamma = \frac{2.464}{M} \exp (9.8 \times 10^{-6} \, MT_c) \tag{7-4.10}$$

For these last two categories of compounds, β is obtained from Eq. (7-4.2) i.e.,

$$\beta = \frac{\gamma}{b} - \frac{ah}{b} \tag{7-4.11}$$

Example 7-3   Repeat Example 7-1 by using the Gomez-Thodos vapor-pressure equation.

solution   From Example 7-1, $T_b = 409.3$ K, $T_c = 617.1$ K, $T_{b_r} = 0.663$, $h = 7.024$. Eqs. (7-4.5) and (7-4.6) should be used for ethylbenzene:

$$\beta = 4.26700 - \frac{221.79}{(7.024)^{2.5} \exp [(0.03848)(7.024)^{2.5}]} + \frac{3.8126}{\exp (2272.44/7.024^3)}$$

$$= -4.2727$$

$$m = 0.78425 \exp [(0.089315)(7.024)] - \frac{8.5217}{\exp [(0.74826)(7.024)]}$$

$$= 1.4242$$

Equations (7-4.2) to (7-4.4) give

$$a = \frac{1 - 1/0.663}{(0.663)^7 - 1} = 0.53863$$

$$b = \frac{1 - 1/(0.663)^{1.4242}}{0.663^7 - 1} = 0.8430$$

$$\gamma = (0.53863)(7.024) + (0.8430)(-4.2727)$$

$$= 0.18143$$

Equation (7-4.1) becomes

$$\ln P_{vpr} = -4.2727\left(\frac{1}{T_r^{1.4242}} - 1\right) + (0.18143)(T_r^7 - 1)$$

T, K	T_r	Vapor pressure, bar Calc.	Vapor pressure, bar Exp.	$\dfrac{P_{calc} - P_{exp}}{P_{exp}} \times 100$
347.2	0.563	0.135	0.133	1.0
460	0.745	3.320	3.325	-0.2

Example 7-4   Use the Gomez-Thodos method to estimate the vapor pressure of isopropanol at 450 K. The literature value is 16.16 bar [6].

solution   For isopropanol, from Appendix A, $M = 60.096$, $T_b = 355.4$ K, $T_c = 508.3$ K, and $P_c = 47.6$ bar. From Eqs. (7-2.5), (7-4.9), and (7-4.10), with $T_{b_r} = 355.4/508.3 = 0.699$,

$$h = 0.699 \frac{\ln (47.6/1.01325)}{1 - 0.699} = 8.948$$

$$m = 0.0052(60.096)^{0.29}(508.3)^{0.72} = 1.515$$

$$\gamma = \frac{2.464}{60.096} \exp [(9.8 \times 10^{-6})(60.096)(508.3)] = 0.0553$$

From Eqs. (7-4.2), (7-4.3), and (7-4.11),

$$a = \frac{1 - 1/0.699}{(0.699)^7 - 1} = 0.469$$

$$b = \frac{1 - 1/(0.699)^{1.515}}{(0.699)^7 - 1} = 0.785$$

$$\beta = 0.0553/0.785 - \frac{(0.469)(8.948)}{0.785} = -5.276$$

From Eq. (7-4.1), with $T_r = 450/508.3 = 0.885$,

$$\ln P_{vp_r} = -5.276 \left(\frac{1}{0.885^{1.515}} - 1 \right) + (0.0553)(0.885^7 - 1) = -1.101$$

$$P_{vp} = 47.6 \exp (-1.101) = 15.83 \text{ bar}$$

$$\text{Error} = \frac{15.83 - 16.16}{16.16} \times 100 = -2.1\%$$

7-5 Vapor Pressure Estimation with Two Reference Fluids

In the Lee-Kesler method, a fluid's properties are obtained by interpolating between the properties of a simple fluid ($\omega = 0$) and a reference fluid (octane with $\omega = 0.3978$). Several authors [11, 84] have suggested that the simple fluid be replaced by a real fluid. This leads to Eq. (3-7.5) and, when written for vapor pressures, gives

$$\ln P_{vp_r} = \ln P_{vp_r}^{(R1)} + (\ln P_{vp_r}^{(R2)} - \ln P_{vp_r}^{(R1)}) \frac{\omega - \omega^{(R1)}}{\omega^{(R2)} - \omega^{(R1)}} \qquad (7\text{-}5.1)$$

The superscripts R1 and R2 refer to the two reference substances. Ambrose and Patel [8] used either propane and octane or benzene and pentafluorotoluene as the reference fluids. In Eq. (7-5.1), all vapor pressures are calculated at the reduced temperature of the substance whose vapor pressure is being predicted. Reduced vapor pressures for the reference substances were calculated with the Wagner equation in the form

$$\ln P_{vp_r} = \frac{a\tau + b\tau^{1.5} + c\tau^3 + d\tau^6}{T_r} \qquad (7\text{-}5.2)$$

where $\tau = 1 - T_r$. Values of the constants a, b, c, and d for these four reference fluids are given in Table 7-1 as well as Appendix A. Equation (7-5.1) is written to estimate vapor pressures. However, if two or more vapor pressures are known in addition to T_c and ω, Eq. (7-5.1) can be used to estimate the critical pressure. Ambrose and Patel [8] have examined this application and report average errors in P_c of about 2 percent for 65 compounds. This is as good as the methods in Chapter 2. When at least three vapor pressures are known, it is mathematically possible to estimate

TABLE 7-1   Constants for Eq. (7-5.2) for Four Reference Fluids [8]

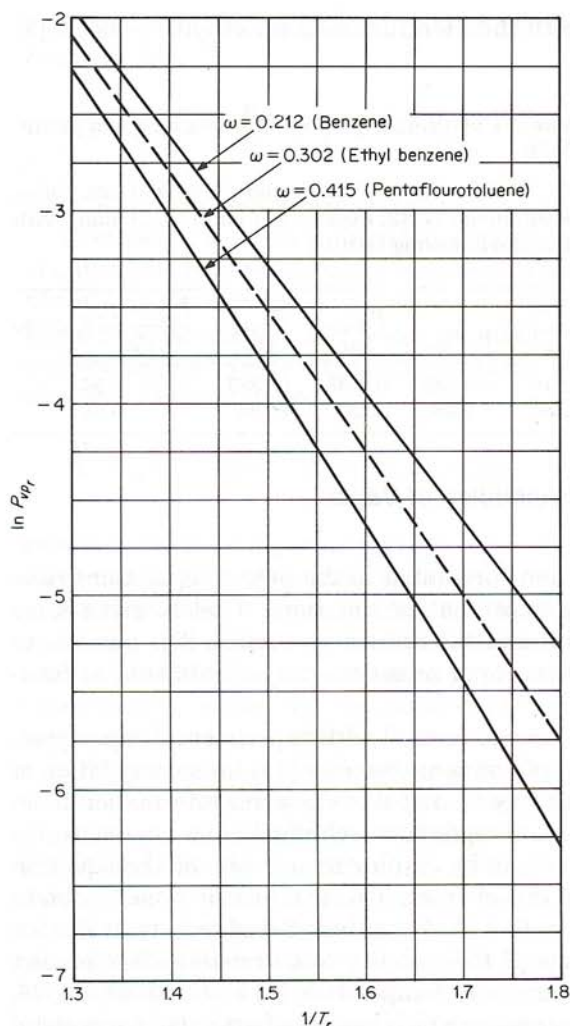| Substance	T_c, K	P_c, bar	ω	a	b	c	d
Propane	369.85	42.4535	0.153	-6.72219	1.33236	-2.13868	-1.38551
Octane	568.81	24.8617	0.398	-7.91211	1.38007	-3.80435	-4.50132
Benzene	562.16	48.9794	0.212	-6.98273	1.33213	-2.62863	-3.33399
Pentafluoro-toluene	566.52	31.2481	0.415	-8.05688	1.46673	-3.82439	-2.78727

Figure 7-2 Vapor pressure prediction for ethylbenzene by the two-reference-fluid method; ——— from Eq. (7-5.2); — — from Eq. (7-5.1).

T_c also, but Ambrose and Patel [8] recommended this not be done. It should be obvious that, when using Eq. (7-5.1), more reliable estimates will be obtained when

$$\omega^{(R1)} < \omega < \omega^{(R2)} \tag{7-5.3}$$

This case represents an interpolation in the acentric factor rather than an extrapolation. Use of Eq. (7-5.1) to estimate vapor pressures is illustrated by Example 7-5 and Fig. 7-2. Within the accuracy of the graph, the dashed

line in Fig. 7-2 coincides with the literature data for ethylbenzene in [3] and [102].

Example 7-5 Repeat Example 7-1 by using Eq. (7-5.1) and benzene and penta-fluorotoluene as reference fluids.

solution For ethylbenzene, $T_c = 617.1$ K, $\omega = 0.302$, and $P_c = 36.0$ bar. Using benzene as R1 and pentafluorotoluene as R2, Eqs. (7-5.1) and (7-5.2) along with the values in Table 7-1 lead to the following results.

T, K	$1/T_r$	$\ln P_{vpr}^{(R1)}$	$\ln P_{vpr}^{(R2)}$	$\ln P_{vpr}$	P_{vpcalc}, bar	P_{vpexp}, bar	$\dfrac{P_{calc} - P_{exp}}{P_{exp}} \times 100$
347.2	1.777	-5.174	-6.110	-5.589	0.1346	0.1333	0.96
460	1.342	-2.216	-2.586	-2.380	3.333	3.325	0.24

7-6 Correlation and Extrapolation of Vapor Pressure Data

Most vapor pressure equations presented in the preceding sections have been introduced primarily as estimating equations. That is, given some data such as a boiling point and the critical properties, it is possible to develop the constants so that vapor pressures can be estimated as functions of temperature.

Upon occasion, however, one is favored with experimental vapor pressure data over a wide range of temperatures (see [15] for a compilation of vapor pressure data), and it may be useful to store this information in an analytical form. Using standard regression techniques, one can determine the best values of the constants by employing any one of the equation forms introduced earlier in this chapter. This is routinely done to obtain the Antoine constants in Eq. (7-3.1). A number of studies have evaluated different equations in terms of their ability to correlate and/or predict vapor pressures over wide ranges of temperature [1, 5, 37, 53, 57, 62, 76, 92a, 95, 96, 103, 106]. One equation which has been particularly successful is the Wagner equation. In the procedure originally proposed by Wagner [96], the form of the equation was variable. Equation (7-5.2) is the simplest form which arises from Wagner's analysis; it has come to be referred to as the Wagner equation, even though a more complex form is superior for water [97, 98], ammonia [12], and oxygen [95]. In all situations in which a form of it was compared to other vapor pressure equations [5, 53, 62, 95, 96], the Wagner equation was selected as the best equation. McGarry [62] has determined values for a, b, c, and d for a number of compounds, and many of those values are listed in Appendix A. For compounds for which ample data are available, P_c was treated as an adjustable parameter; and in some of these cases, this is the value listed for P_c in Appendix A. When Wagner constants were not available for a particular

compound, Antoine constants, or constants for the Frost-Kalkwarf-Thodos equation

$$\ln P_{vp} = A - \frac{B}{T} + C \ln T + \frac{DP_{vp}}{T^2} \qquad (7\text{-}6.1)$$

have been tabulated in Appendix A.

An equation's ability to correlate data depends directly on the number of adjustable parameters in the equation. When one has only a small number of data, or requires computational simplicity, one might use only three adjustable parameters. The Antoine equation (7-3.1) is the most common, but not the best, three-parameter equation. McGarry [62] found that the modified Miller equation

$$\ln P_{vp_r} = -\frac{A}{T_r}[1 - T_r^2 + B(3 + T_r)(1 - T_r)^3] \qquad (7\text{-}6.2)$$

gave a better fit to experimental data than did the Antoine equation. The three fitted constants in Eq. (7-6.2) are A, B, and P_c ($P_{vp_r} = P_{vp}/P_c$).

Sometimes vapor pressure data are available over a limited temperature range and one wishes to extrapolate the data to higher or lower temperatures. The Antoine equation does not reproduce the correct shape of a vapor pressure curve over the entire temperature range and should not be used for extrapolation [49]. If it is used to calculate vapor pressures outside the range of temperatures listed in Appendix A, serious errors may result. The Wagner equation may be used to extrapolate data because of the manner in which the constants have been determined. In addition to requiring a best fit of existing vapor pressure data, the equation is constrained so as to generate a "reasonable shape" for the vapor pressure curve from a reduced temperature of 0.5 up to the critical point. The correct shape of a vapor pressure curve is well documented [4, 20, 62, 99], and several authors have demonstrated the use of the constrained fit method [4, 62]. Ambrose et al. [4] have shown that the constrained fit technique may be used to estimate critical pressures with an accuracy comparable to that obtained with Eq. (7-5.1). The Wagner constants in Appendix A are also from a constrained fit [62]. The Wagner equation may not extrapolate well to reduced temperatures below 0.5.

Vapor pressure data below reduced temperatures of about 0.5 are sparse, although Carruth and Kobayashi [19] give vapor pressure data for the normal paraffins ethane through n-decane down to their triple points. Low-temperature vapor pressures are usually obtained by integrating the Clausius-Clapeyron equation. King and Al-Najjar [50] have done this integration along the saturation curve for eight normal alkanes, and Ambrose and Davies [7] have used the method for nine other organic compounds. These studies establish reliable values for 17 compounds that

may be used as reference fluid values in the two-reference-fluid method, Eq. (7-5.1), to estimate vapor pressures of additional compounds. Mosselman et al. [65] have presented the Clausius-Clapeyron equation in the form of an exact differential so that integration is path-independent. One integrated form they present is

$$\frac{1}{T_1} \int_{P_0}^{P_1} \Delta V_v(P, T_1) \, dP + \int_{1/T_0}^{1/T_1} \left[\int_{T_0}^{T} \Delta C_{p_v}(P_0, T) \, dT \right] dT^{-1}$$
$$= \Delta H_v(P_0, T_0) \, (T_0^{-1} - T_1^{-1}) \quad (7\text{-}6.3)$$

In Eq. (7-6.3), ΔH_v and P_0 are the enthalpy of vaporization and vapor pressure at T_0. P_1 is the vapor pressure to be calculated at T_1. ΔV_v is the vapor volume minus the liquid volume at P and T_1; ΔC_{p_v} is the vapor heat capacity minus the liquid heat capacity at P_0 and T. If ΔV_v and ΔC_{p_v} data are available or can be estimated, Eq. (7-6.3) provides a thermodynamically sound extrapolation method. Equation (7-6.3) is particularly useful for low temperatures and pressures when deviations from ideal-gas behavior are small for the vapor phase.

7-7 Discussion and Recommendations for Vapor Pressure Estimation and Correlation

Starting from the Clausius-Clapeyron equation (7-2.2), we have shown only a few of the many vapor pressure equations which have been published. We have emphasized those which appear to be most accurate and general. Properties required for the different estimation equations are T_b, M, and T_c for Gomez-Thodos and ω and T_c for the two-reference-fluid and Lee-Kesler methods. It is amazing how well these techniques predict vapor pressures over wide ranges of temperature with this little input. We show in Table 7-2 a detailed comparison of calculated and experimental vapor pressures for acetone for the estimation techniques described in this chapter. The range shown is from 0.04 bar to the critical point, 47 bar. The least accurate is, as expected, the Clapeyron equation, especially at lower temperatures.

The Antoine equation should not be used above 2.0 to 2.7 bar when the constants are obtained from experimental data below that pressure. In the range for which the constants are applicable, it is very accurate. Of the methods shown in Table 7-2 the Wagner equation is the most accurate, although all the predictive methods, i.e., Lee-Kesler, Gomez-Thodos, and the two-reference fluid methods, perform satisfactorily.

The methods presented in this chapter cannot be used to estimate vapor pressures of high-molecular-weight compounds if the normal boiling points cannot be determined. When no vapor pressure data exist but the molecular structure of a compound is known, the UNIFAC group con-

TABLE 7-2 Comparison between Calculated and Experimental Vapor Pressures for Acetone

T, K	T_r	P_{vp} (exp.), bar[b]	Clapeyron, Eq. (7-2.4)	Antoine, Eq. (7-3.1)[c]	Wagner Eq. (7-5.2)	Gomez and Thodos Eq. (7-4.1)	Two reference fluids[d] Eq. (7-5.1)	Lee and Kesler, Eq. (7-2.6)
				Percent error[a]				
259.2	0.510	0.04267	24	1.6	0.2	1.1	−5.5	−7.9[e]
273.4	0.538	0.09497	15	0.3	−0.1	0.2	−3.9	−6.2
290.1	0.571	0.21525	8.3	−0.1	0.2	0.1	−2.0	−3.7
320.5	0.631	0.74449	1.5	−0.7	0.1	0.1	0	−0.2
350.9	0.691	2.01571	−1.0	−0.6	0	0.3	0.8	1.9
390.3	0.768	5.655	−1.5	0.1	0.2	0.8	1.3	2.2
446.4	0.878	17.682	−0.3	−0.5	0	0.6	0.6	0.7
470.6	0.926	26.628	0.5	1.5[f]	−0.1	0.3	−0.2	0.3
508.1	1.00	47.000		−4.5[f]				

[a]Percent error = [(calc. − exp.)/exp.] × 100.
[b]Experimental data from Ref. 9.
[c]ln P_{vp} = 10.0311 − 2940.45/(T − 35.93), P_{vp} is in bars.
[d]Reference fluids are propane and octane.
[e]ω calculated from Eq. (2-3.4) (ω = 0.301) rather than obtained from Appendix A (ω = 0.304).
[f]Constants not applicable at high reduced temperature.

tribution method [19a, 45, 104] or the group contribution methods [16, 43, 78] similar to the method developed by Prausnitz and coworkers [26, 59] can be used. White [100] has used the molecular connectivity [48] to correlate the normal boiling point and ΔH_{vb} for polycyclic aromatic hydrocarbons, and Willman and Teja [102a] have correlated constants in the Wagner equation with effective carbon numbers. When no vapor pressure data are available and when one is uncertain of the molecular structure of a compound, or a petroleum fraction, the SWAP equation [27, 60, 81] may be used.

Recommendations

If constants for a particular compound are available in Appendix A, use them along with the appropriate equation. The Antoine equation should not be used for temperatures outside the range listed in Appendix A. The Wagner equation may be extrapolated to higher temperatures with confidence. It may be used down to a reduced temperature of 0.5 or to the value of T_{min} listed in Appendix A; extrapolations to lower temperatures may lead to unacceptable errors. For reduced temperatures below 0.5, the Lee-Kesler equation (7-2.6) or the two-reference-fluid method, Eq. (7-5.1), is recommended. Except for alcohols, errors should be less than 30 percent. If higher accuracy is required, at low temperatures, vapor pressures may be calculated with Eq. (7-6.2) or as in Refs. 7 and/or 50. For predictions for polar compounds at reduced temperatures between 0.5 and 1.0, the two-reference-fluid or Gomez-Thodos methods are recommended. If no data are available for a compound, and the compound's normal boiling point is unknown, one of the group contribution methods mentioned above may be used. In that event, however, calculated results are not likely to be highly accurate.

7-8 Enthalpy of Vaporization of Pure Compounds

The enthalpy of vaporization ΔH_v is sometimes referred to as the latent heat of vaporization. It is the difference between the enthalpy of the saturated vapor and that of the saturated liquid at the same temperature.

Because of the forces of attraction between the molecules of the liquid, the molecules escaping are those of higher than average energy. The average energy of the remaining molecules in the liquid is reduced, and energy must be supplied to maintain the temperature constant. This is the internal energy of vaporization ΔU_v. Work is done on the vapor phase as vaporization proceeds, since the vapor volume increases if the pressure is maintained constant at P_{vp}. This work is $P_{vp}(V_g - V_L)$. Thus

$$\Delta H_v = \Delta U_v + P_{vp}(V_g - V_L) = \Delta U_v + RT(Z_g - Z_L) \tag{7-8.1}$$
$$= \Delta U_v + RT\,\Delta Z_v$$

Many estimation methods for ΔH_v can be traced to Eq. (7-2.2), where it is shown that ΔH_v is related to the slope of the vapor pressure–temperature curve. Other methods are based on the law of corresponding states. We review the more accurate techniques in Secs. 7-9 to 7-12; recommendations are presented in Sec. 7-13. Literature references to experimental and calculated values of ΔH_v have been compiled in [83].

It is often difficult to trace the origin of many "experimental" enthalpies of vaporization. A few have been determined from calorimetric measurements, but in a large number of cases the so-called experimental value was obtained directly from Eq. (7-2.2). Some technique was employed to determine ΔZ_v separately, and also $(d \ln P_{vp})/dT$ was found by numerical differentiation of experimental vapor pressure data or by differentiating some P_{vp}-T correlation analytically. An example of this latter approach can be found in the 1971 reissue of the API Tables [101]. Enthalpies of vaporization were determined by using Eq. (7-2.2), where dP_{vp}/dT was found from the Antoine vapor pressure equation (Sec. 7-3); the saturated vapor compressibility factor was estimated from a virial equation of state (Sec. 3-5); and experimental data were employed for saturated liquid compressibility factors.

An element of uncertainty is introduced in using any analytical vapor pressure–temperature equation to obtain accurate values of slopes dP_{vp}/dT. The constants in the equation may be optimum for correlating vapor pressures, but it does not necessarily follow that these same constants give the best fit for computing slopes. With the Antoine equation, for example, different sets of the constants A, B, and C can represent a set of experimental data satisfactorily. But differentiation eliminates A and increases the importance of C. Uncertainties in C lead directly to uncertainties in ΔH_v.

Since so few calorimetric measurements of ΔH_v are available, there is little that can be done to rectify the problem. A critical survey of reported ΔH_v values would, nevertheless, be of value, since one would like to avoid the logical pitfalls of comparing estimated values of ΔH_v with values estimated by other approximate methods and then making recommendations based on such a comparison.

7-9 Estimation of ΔH_v from the Law of Corresponding States

Equation (7-2.1), in reduced form, becomes

$$d \ln P_{vp_r} = \frac{-\Delta H_v}{RT_c \, \Delta Z_v} \, d \, \frac{1}{T_r} \tag{7-9.1}$$

The reduced enthalpy of vaporization $-\Delta H_v/RT_c$ is a function of $(d \ln P_{vp_r})/d(1/T_r)$ and ΔZ_v; both these parameters are commonly assumed to

be functions of T_r or P_{vp}, and some third parameter such as ω, Z_c, or h. A number of correlations based on this approach have been suggested.

Pitzer acentric factor correlation [70]

Pitzer et al. have shown that ΔH_v can be related to T, T_r, and ω by an expansion similar to that used to estimate compressibility factors, Eq. (3-3.1), i.e.,

$$\frac{\Delta H_v}{T} = \Delta S_v^{(0)} + \omega \, \Delta S_v^{(1)} \tag{7-9.2}$$

where $\Delta S_v^{(0)}$ and $\Delta S_v^{(1)}$ are expressed in entropy units, for example, J/(mol·K), and are functions only of T_r. Multiplying Eq. (7-9.2) by T_r/R gives

$$\frac{\Delta H_v}{RT_c} = \frac{T_r}{R}(\Delta S_v^{(0)} + \omega \, \Delta S_v^{(1)}) \tag{7-9.3}$$

Thus $\Delta H_v/RT_c$ is a function only of ω and T_r. From the tabulated $\Delta S_v^{(0)}$ and $\Delta S_v^{(1)}$ functions given by Pitzer et al. and extended to low reduced temperatures by Carruth and Kobayashi [18], Fig. 7-3 was constructed. For a close approximation, an analytical representation of this correlation for $0.6 < T_r \le 1.0$ is

$$\frac{\Delta H_v}{RT_c} = 7.08(1 - T_r)^{0.354} + 10.95\omega(1 - T_r)^{0.456} \tag{7-9.4}$$

The effect of temperature on ΔH_v is similar to that suggested by Watson (see Sec. 7-12). Nath [68] has presented an equation similar to Eq. (7-9.4) for $0.5 < T_r < 0.7$. To use the Lee-Kesler method to obtain values for $\Delta S_v^{(0)}$ and $\Delta S_v^{(1)}$, the vapor pressure is determined with Eq. (7-2.6) and $H - H°$ is evaluated for both liquid and vapor. The difference in these two enthalpy departure functions is ΔH_v. Gupte and Daubert [38] report good results with this approach; the approach is given graphically in [47].

Example 7-6 By using the Pitzer et al. corresponding states correlation, estimate the enthalpy of vaporization of propionaldehyde at 321 K. The literature value is 28280 J/mol [22].

solution From Appendix A, $T_c = 496$ K and $\omega = 0.313$. $T_r = 321/496 = 0.647$, and from Eq. (7-9.4)

$$\frac{\Delta H_v}{RT_c} = (7.08)(1 - 0.647)^{0.354} + (10.95)(0.313)(1 - 0.647)^{0.456}$$

$$= 7.03$$

$$\Delta H_v = (7.03)(8.314)(496) = 29{,}000 \text{ J/mol}$$

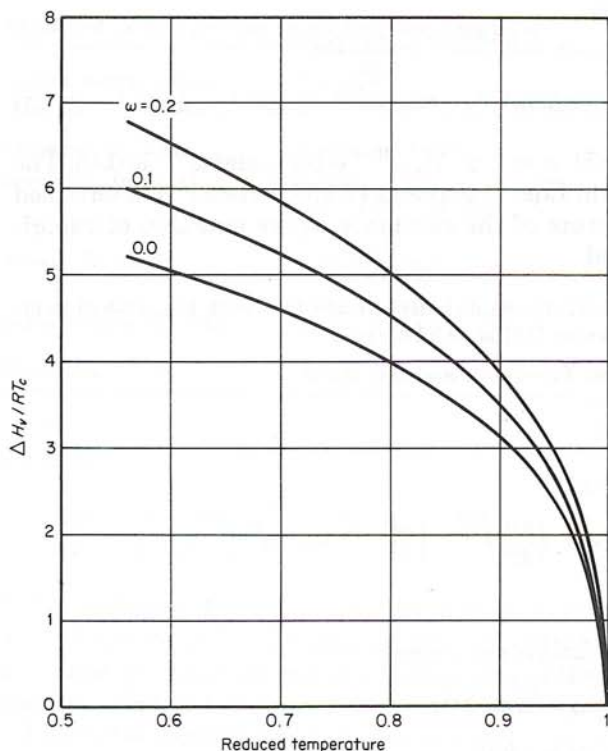$$\text{Error} = \frac{29{,}000 - 28{,}280}{28{,}280} \times 100 = 2.5\%$$

Figure 7-3 Plot of Pitzer et al. correlation for enthalpies of vaporization.

Two-reference-fluid method

Sivaraman et al. [80] have used the two-reference-fluid method to calculate enthalpies of vaporization of coal compounds between their freezing points and critical points. An equation developed by Torquato and Stell [90] was used for the reference fluids, benzene and carbazole. These equations are

$$\frac{\Delta H_v}{RT_c} = \left(\frac{\Delta H_v}{RT_c}\right)^{(R1)} + \left(\frac{\omega - \omega^{(R1)}}{\omega^{(R2)} - \omega^{(R1)}}\right)\left[\left(\frac{\Delta H_v}{RT_c}\right)^{(R2)} - \left(\frac{\Delta H_v}{RT_c}\right)^{(R1)}\right] \qquad (7\text{-}9.5)$$

For benzene,

$$\left(\frac{\Delta H_v}{RT_c}\right)^{(R1)} = 6.537\tau^{1/3} - 2.467\tau^{5/6} - 77.521\tau^{1.208}$$

$$+ 59.634\tau + 36.009\tau^2 - 14.606\tau^3 \qquad (7\text{-}9.6)$$

The quantity $(\Delta H_v/RT_c)^{(R2)} - (\Delta H_v/RT_c)^{(R1)}$ in Eq. (7-9.5) is the difference in the reduced enthalpies of vaporization of carbazole and benzene and is given by

$$\left(\frac{\Delta H_v}{RT_c}\right)^{(R2)} - \left(\frac{\Delta H_v}{RT_c}\right)^{(R1)} = -0.133\tau^{1/3} - 28.215\tau^{5/6}$$

$$-82.958\tau^{1.208} + 99.000\tau + 19.105\tau^2 - 2.796\tau^3 \quad (7\text{-}9.7)$$

In Eqs. (7-9.6) and (7-9.7), $\tau = 1 - T_r$, $\omega^{(R1)}$ is 0.21, and $\omega^{(R2)}$ is 0.46. The same value of τ is used in Eqs. (7-9.6) and (7-9.7), where τ is determined at the reduced temperature of the substance whose enthalpy of vaporization is being estimated.

Example 7-7 Calculate ΔH_v for naphthalene at 553.15 K with Eqs. (7-9.5) to (7-9.7). The experimental value [80] is 39.82 kJ/mol.

solution For naphthalene, $T_c = 748.4$ and $\omega = 0.302$.

$$\tau = 1 - \frac{553.15}{748.4} = 0.2609$$

From Eqs. (7-9.6 and (7-9.7)

$$\left(\frac{\Delta H_v}{RT_c}\right)^{(R1)} = 5.840 \quad \text{and} \quad \left(\frac{\Delta H_v}{RT_c}\right)^{(R2)} - \left(\frac{\Delta H_v}{RT_c}\right)^{(R1)} = 1.426$$

Equation (7-9.5) gives

$$\frac{\Delta H_v}{RT_c} = 5.840 + \left(\frac{0.302 - 0.21}{0.46 - 0.21}\right)(1.426) = 6.365$$

$$\Delta H_v = (6.365)(8.314)(748.4) = 39{,}600 \text{ J/mol} = 39.6 \text{ kJ/mol}$$

$$\text{Error} = \frac{39.6 - 39.82}{39.82} \times 100 = -0.6\%$$

7-10   Estimation of ΔH_v from Vapor Pressure Equations

The vapor pressure correlations covered in Secs. 7-2 to 7-6 can be used to estimate enthalpies of vaporization. From Eq. (7-9.1), we can define a dimensionless group ψ as

$$\psi \equiv \frac{\Delta H_v}{RT_c \, \Delta Z_v} = \frac{-d \ln P_{vpr}}{d(1/T_r)} \quad (7\text{-}10.1)$$

By differentiating the vapor pressure equations discussed earlier, we can obtain various expressions for ψ. These are shown in Table 7-3. To use the expressions, one must refer back to the reference vapor pressure equation earlier in the chapter for the definition of the various parameters.

In Fig. 7-4, we show experimental values of ψ for propane. These were calculated from smoothed values tabulated in Refs. 24 and 105. Note the pronounced minimum in the curve around $T_r = 0.8$. Since

$$\psi = \frac{-d \ln P_{vpr}}{d(1/T_r)} \quad (7\text{-}10.7)$$

TABLE 7-3 ψ Values from Vapor Pressure Equations

Vapor pressure equation	$\psi = \dfrac{\Delta H_v}{RT_c\,\Delta Z_v}$	
Clapeyron, Eq. (7-2.4)	h, defined in Eq. (7-2.5)	(7-10.2)
Lee-Kesler, Eq. (7-2.6)	$6.09648 - 1.28862T_r + 1.016T_r^7 + \omega(15.6875 - 13.4721T_r + 2.615T_r^7)$	(7-10.3)
Antoine, Eq. (7-3.1)	$\dfrac{B}{T_c}\left(\dfrac{T_r}{T_r + C/T_c}\right)^2$	(7-10.4)
Gomez-Thodos, Eq. (7-4.1)	$7\gamma T_r^6 - \dfrac{\beta m}{T_r^{m-1}}$	(7-10.5)
Wagner, Eq. (7-5.2)	$-a + b\tau^{0.5}(0.5\tau - 1.5) + c\tau^2(2\tau - 3) + d\tau^5(5\tau - 6)$	(7-10.6)

we have

$$\frac{d\psi}{dT_r} = \frac{1}{T_r^2}\frac{d^2 \ln P_{vp_r}}{d(1/T_r)^2} \tag{7-10.8}$$

At low values of T_r, $d\psi/dT_r < 0$, so that $(d^2 \ln P_{vp_r})/d(1/T_r)^2$ is also < 0. At high values of T_r, the signs reverse. When $d\psi/dT_r = 0$, an inflection point results. Thus the general (though exaggerated) shape of a log vapor pressure–inverse temperature curve is that shown in Fig. 7-5.

Figure 7-6 illustrates how the various vapor pressure equations can predict the shape of Fig. 7-4. Except for the Clapeyron equation (where ψ is a constant equal to h), the other equations show a remarkable fit to the value of ψ calculated from literature data for propane. The Antoine equation does not predict the ψ–T_r minimum, and the calculated curve was drawn only to $T_r = 0.83$. The curve generated with the Wagner constants
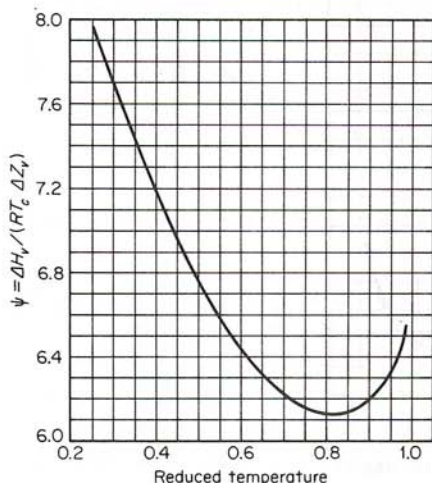

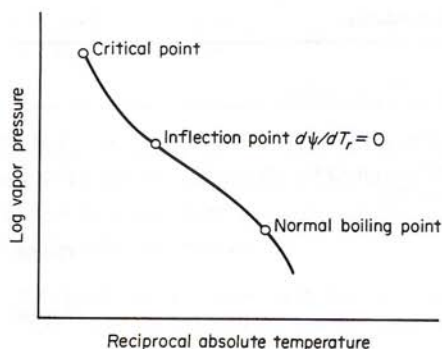**Figure 7-4** Literature values of ψ for propane.

Figure **7-5** Schematic vapor pressure plot.

in Appendix A and Eq. (7-10.6) is not shown in Fig. 7-6 because it coincides with the literature values over the T_r range shown in the figure.

Other comparisons also produced good results. We may, therefore, recommend these vapor pressure correlations to predict ψ and thus ΔH_v. However, accurate values of ΔZ_v must be available. To date, available correlations for ΔZ_v are not accurate. ΔZ_v is determined best as a difference in the Z values of saturated vapor and saturated liquid. For saturated liquid, the methods in Chap. 3 are appropriate. For the specific saturated
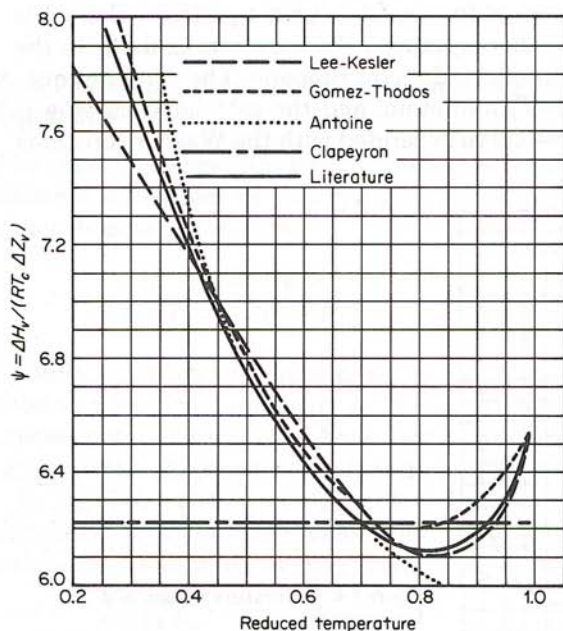

Figure 7-6 Comparison between calculated and experimental values of $\Delta H_v/(RT_c \, \Delta Z_v)$ for propane.

volumes of nonpolar materials, the following equation presented by Thompson and Sullivan [86] may be used from the triple point to the critical point

$$(1 - P_{vp_r})^\beta = |1 - V_r^{-\lambda}| \tag{7-10.9}$$

V_r is the reduced saturated vapor volume; values of β and λ are listed in [86] or may be estimated by

$$\beta = 0.346 - 0.067\omega \tag{7-10.10}$$

$$\lambda = 1 + 0.085(1 + 0.19\omega)^{-8} \tag{7-10.11}$$

Equations (7-10.9) to (7-10.11) gave errors which were usually less than 3 percent but could be as high as 10 percent.

7-11 ΔH_v at the Normal Boiling Point

A pure component constant that is occasionally used in property correlations is the enthalpy of vaporization at the normal boiling point ΔH_{vb}. Any one of the correlations discussed in Secs. 7-8 to 7-10 can be used for this state where $T = T_b$, $P = 1.01$ bar. We discuss some of the techniques below. In addition, several special estimation methods are suggested.

ΔH_{vb} from vapor pressure relations

In Table 7-3, we show equations for $\psi \equiv \Delta H_v/(RT_c \Delta Z_v)$ as determined from a number of the more accurate vapor pressure equations. Each can be used to determine ψ (T_b). With ψ (T_b) and ΔZ_v (T_b), ΔH_{vb} can be determined.

Special mention should be made when the Clapeyron equation is used to calculate ψ [see Eq. (7-10.2) in Table 7-3]. Here, ψ is equal to h regardless of T_r, that is,

$$\psi (T_r) = \psi (T_b) = T_{b_r} \frac{\ln (P_c/1.01325)}{1 - T_{b_r}} \tag{7-11.1}$$

and
$$\Delta H_{vb} = RT_c \Delta Z_{vb} \left(T_{b_r} \frac{\ln (P_c/1.01325)}{1 - T_{b_r}} \right) \tag{7-11.2}$$

Equation (7-11.2) has been widely employed to make rapid estimates of ΔH_{vb}; usually, in such cases, ΔZ_{vb} is set equal to unity. In this form, it has been called the Giacalone equation [32]; extensive testing of this simplified form indicates that it normally overpredicts ΔH_{vb} by a few percent. Correction terms have been suggested [30, 52] to improve the accuracy of the Giacalone equation, but better results are obtained with other relations, noted below.

TABLE 7-4   Comparison between Calculated and Experimental Values of ΔH_{vb}

		Average absolute percent error			
Class of compounds	Number of compounds	Giacalone, Eq. (7-11.2)	Riedel, Eq. (7-11.3)	Chen, Eq. (7-11.4)	Vetere, Eq. (7-11.5)
Saturated hydrocarbons	22	2.9	0.9	0.4	0.4
Unsaturated hydrocarbons	8	2.4	1.4	1.2	1.2
Cycloparaffins and aromatics	12	1.1	1.3	1.2	1.1
Alcohols	7	3.6	4.0	4.0	3.8
Nitrogen and sulfur compounds (organic)	10	1.6	1.7	1.7	1.9
Halogenated compounds	10	1.3	1.6	1.5	1.5
Rare gases	5	8.4	2.1	2.2	2.5
Nitrogen and sulfur compounds (inorganic)	4	3.0	2.7	2.7	2.1
Inorganic halides	4	0.6	1.4	1.4	0.9
Oxides	6	6.9	4.4	4.9	4.6
Other polar compounds	6	2.2	1.5	1.8	1.6
Total	94	2.8	1.8	1.7	1.6

Riedel method

Riedel [77] modified Eq. (7-11.2) slightly and proposed that

$$\Delta H_{vb} = 1.093 R T_c \left[T_{br} \frac{\ln P_c - 1.013}{0.930 - T_{br}} \right] \tag{7-11.3}$$

When tested as shown in Table 7-4, errors are almost always less than 2 percent.

Chen method

Chen [21] used Eq. (7-9.3) and a similar expression proposed by Pitzer et al. to correlate vapor pressures so that the acentric factor is eliminated. He obtained a relation between ΔH_v, P_{vpr}, and T_r. When applied to the normal boiling point,

$$\Delta H_{vb} = R T_c T_{br} \frac{3.978 T_{br} - 3.958 + 1.555 \ln P_c}{1.07 - T_{br}} \tag{7-11.4}$$

This correlation was tested with the results shown in Table 7-4. The accuracy is similar to that of the Riedel equation (7-11.3). In a more complete test, Chen compared estimated ΔH_{vb} with literature values for 169 materials and found an average error of 2.1 percent.

Vetere method

Vetere [91] proposed a relation similar to the one suggested by Chen:

$$\Delta H_{vb} = RT_c T_{br} \frac{0.4343 \ln P_c - 0.69431 + 0.89584 T_{br}}{0.37691 - 0.37306 T_{br} + 0.15075 P_c^{-1} T_{br}^{-2}} \qquad (7\text{-}11.5)$$

As shown in Table 7-4, this empirical equation is capable of providing a good estimate of ΔH_{vb}; errors are normally less than 2 percent.

Other methods

A number of other methods for estimating ΔH_{vb} have been proposed. None appears to offer any significant advantages over those given above. Miller [64] used an earlier version of the Riedel-Plank-Miller vapor pressure equation to determine ψ and then, with $\Delta Z_{vb} \approx 1 - 0.97/P_c T_{br}$, he obtained a relation for ΔH_{vb} in terms of T_{br} and P_c. The final result is more complex than Eqs. (7-11.3) to (7-11.5), but the results are similar.

Ibrahim and Kuloor [44] presented two correlations for ΔH_{vb} in which the molecular weight or liquid volume is employed as the independent variable. Specific constants are required for various homologous series. Ogden and Lielmezs [69] proposed a similar relation, but in this case the Altenburg quadratic mean radius was used. The latter term reflects the mass distribution in a molecule. Procopio and Su [73] and Viswanath and Kuloor [93] have suggested modifications to the Giacalone equation, Eq. (7-11.2). Narsimhan [67] relates ΔH_{vb} to a density function. Various group contribution methods have been proposed to estimate ΔH_{vb} or ΔH_v at 298 K [28, 33, 42, 55, 61].

Comparison of estimated with literature values of ΔH_{vb}

Table 7-4 compares calculated and experimental values of ΔH_{vb} by using the estimation methods described in this section. The Riedel, Pitzer-Chen, and Vetere relations [Eqs. (7-11.3) to (7-11.5)] are convenient and are generally accurate. In every case, T_b, T_c, and P_c must be known or estimated.

Example 7-8 Estimate the enthalpy of vaporization of propionaldehyde at the normal boiling point. The experimental value is 28280 J/mol [22].

solution From Appendix A, $T_b = 321$ K, $T_c = 496$ K, and $P_c = 47.6$ bar. Thus $T_{br} = 0.647$.

RIEDEL METHOD.   With Eq. (7-11.3)

$$\Delta H_{vb} = (1.093)(8.314)(496) \frac{(0.647)(\ln 47.6 - 1.013)}{0.930 - 0.647}$$

$$= 29,370 \text{ J/mol}$$

$$\text{Error} = \frac{29,370 - 28,280}{28,280} \times 100 = 3.8\%$$

GIACALONE METHOD.   With Eq. (7-11.2) and assuming $\Delta Z_{vb} = 1.0$,

$$\Delta H_{vb} = (8.314)(496)\left(\frac{0.647 \ln 47.6/1.01325}{1 - 0.647}\right)$$

$$= 29,100 \text{ J/mol}$$

$$\text{Error} = \frac{29,100 - 28,280}{28,280} \times 100 = 2.9\%$$

CHEN METHOD.   From Eq. (7-11.4)

$$\Delta H_{vb} = \frac{(8.314)(496)(0.647)[(3.978)(0.647) - 3.958 + 1.555 \ln 47.6]}{1.07 - 0.647}$$

$$= 29,160 \text{ J/mol}$$

$$\text{Error} = \frac{29,160 - 28,280}{28,280} \times 100 = 3.1\%$$

VETERE METHOD.   From Eq. (7-11.5)

$$\Delta H_{vb} = (8.314)(496)(0.647) \frac{0.4343 \ln 47.6 - 0.69431 + (0.89584)(0.647)}{0.37691 - (0.37306)(0.647) + (0.15075)(47.6)^{-1}(0.647)^{-2}}$$

$$= 29,140 \text{ J/mol}$$

$$\text{Error} = \frac{29,140 - 28,280}{28,280} \times 100 = 3.0\%$$

7-12   Variation of ΔH_v with Temperature

The latent heat of vaporization decreases steadily with temperature and is zero at the critical point. Typical data are shown in Fig. 7-7. The shapes of these curves agree with most other enthalpy-of-vaporization data.

The variation of ΔH_v with temperature could be determined from any of the ψ relations shown in Table 7-3, although the variation of ΔZ_v with temperature would also have to be specified.

A widely used correlation between ΔH_v and T is the Watson relation [85]

$$\Delta H_{v2} = \Delta H_{v1}\left(\frac{1 - T_{r2}}{1 - T_{r1}}\right)^n \tag{7-12.1}$$

where subscripts 1 and 2 refer to temperatures 1 and 2. A common choice for n is 0.375 or 0.38 [87].

Viswanath and Kuloor [94] recommend that n be obtained by

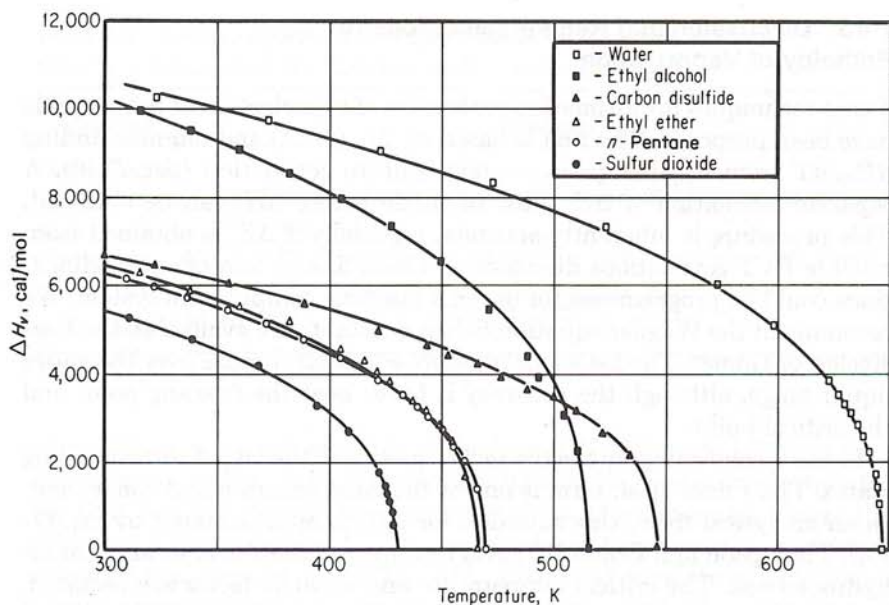$$n = \left(0.00264 \frac{\Delta H_{vb}}{RT_b} + 0.8794\right)^{10} \tag{7-12.2}$$

Figure 7-7 Enthalpies of vaporization.

Fish and Lielmezs [29, 79] suggest a different way to correlate ΔH_v with T:

$$\Delta H_v = \Delta H_{vb} \frac{T_r}{T_{b_r}} \frac{X + X^q}{1 + X^p} \qquad (7\text{-}12.3)$$

where

$$X = \frac{T_{b_r}}{T_r} \frac{1 - T_r}{1 - T_{b_r}} \qquad (7\text{-}12.4)$$

and the parameters q and p are:

	q	p
Liquid metals	0.20957	-0.17467
Quantum liquids*	0.14543	0.52740
Inorganic and organic liquids	0.35298	0.13856

*Helium, hydrogen, deuterium, neon.

Compared with Eq. (7-12.1), with $n = 0.38$, Eq. (7-12.3) predicts slightly smaller values of ΔH_v when $T < T_b$ and somewhat higher when $T > T_b$. For liquid metals and quantum liquids, Eq. (7-12.3) is more accurate than Eq. (7-12.1), but for inorganic and organic liquids, the average errors reported by Fish and Lielmezs for Eqs. (7-12.1) and (7-12.3) were not significantly different.

7-13 Discussion and Recommendations for Enthalpy of Vaporization

Three techniques for estimating enthalpies of vaporization of pure liquids have been proposed. The first is based on Eq. (7-2.1) and requires finding dP_{vp}/dT from a vapor pressure–temperature correlation (Sec. 7-10). A separate estimation of ΔZ_v must be made before ΔH_v can be obtained. This procedure is inherently accurate, especially if ΔZ_v is obtained from reliable PVT correlations discussed in Chap. 3. Any number of modifications could be programmed for use in a machine computation system. We recommend the Wagner equation (when constants are available), the Lee-Kesler, or Gomez-Thodos vapor pressure equations for use over the entire liquid range, although the accuracy is lower near the freezing point and the critical point.

In the second category are the techniques from the law of corresponding states. The Pitzer et al. form is one of the most accurate and convenient. In an analytical form, this equation for ΔH_v is approximated by Eq. (7-9.4). Thompson and Braun [87] also recommend the Pitzer et al. form for hydrocarbons. The critical temperature and acentric factor are required. A second corresponding states method is the two-reference fluid method of Sivaraman et al., Eqs. (7-9.5) to (7-9.7).

The third method is to estimate ΔH_{vb} as recommended in Sec. 7-11 and then scale with temperature with the Watson or Fish-Lielmezs functions discussed in Sec. 7-12.

All three of these techniques are satisfactory, and all yield approximately the same error when averaged over many types of fluids and over large temperature ranges. Fishtine [31], in a separate review of predictive methods of ΔH_v, did not consider the first of the methods discussed above but claimed comparable accuracy for the latter two.

All the methods noted above can be improved in accuracy for special cases. For example, Halm and Stiel [39, 40] have modified the Pitzer et al. correlation for polar fluids at lower reduced temperatures.

Finally, for all correlations discussed, T_c and P_c are required either directly or indirectly. Although these constants are available for many fluids—and can be estimated for most others—there are occasions when one would prefer not to use critical properties. (For example, for some high-molecular-weight materials or for polyhydroxylated compounds, it is difficult to assign reliable values to T_c and P_c.) In such cases, one may have to use an approximate rule for the entropy of vaporization at the normal boiling point and then scale with temperature with the Watson relation (described in Sec. 7-12) with an estimated T_c. Several entropy-of-vaporization rules are described in an earlier edition of this book [75]. One of the more useful of such rules was suggested by Kistiakowsky [51].

$$\frac{\Delta H_{vb}}{T_b} = \Delta S_{vb} = 36.6 + R \ln T_b \qquad (7\text{-}13.1)$$

TABLE 7-5 Vetere's Modification of the Kistiakowsky Equation
$\Delta H_{vb}/T_b = \Delta S_{vb}$, J/(mol·K); T_b in kelvins; M = molecular weight

Type of compound	Correlation
Alcohols, acids, methylamine	$\Delta S_{vb} = 81.119 + 13.083 \log T_b - 25.769 \dfrac{T_b}{M} + 0.146528 \dfrac{T_b^2}{M} - 2.1362 \times 10^{-4} \dfrac{T_b^3}{M}$
Other polar compounds†	$\Delta S_{vb} = 44.367 + 15.33 \log T_b + 0.39137 \dfrac{T_b}{M} + 4.330 \times 10^{-3} \dfrac{T_b^2}{M} - 5.627 \times 10^{-6} \dfrac{T_b^3}{M}$
Hydrocarbons	$\Delta S_{vb} = 58.20 + 13.7 \log M + 6.49 \dfrac{[T_b - (263M)^{0.581}]^{1.037}}{M}$

†For esters, multiply the calculated value of ΔS_{vb} by 1.03.

where T_b is in kelvins and ΔS_{vb} is in J/(mol·K). Fishtine [30] improved the accuracy of Eq. (7-13.1) by employing a multiplicative correction factor that is a function of the compound class. More recently, Vetere [92] proposed a form wherein ΔS_{vb} is correlated as a function of T_b and M; his relations are given in Table 7-5. ΔH_{vb} predicted from these equations is almost always within ±5 percent of the experimental value, and for most cases the error is below 3 percent.

Example 7-9 Repeat Example 7-8 by using the Vetere equation for ΔS_{vb}.

solution From Appendix A, $T_b = 321$ K and $M = 58.08$. Using the second equation in Table 7-5 gives

$$\Delta S_{vb} = 44.376 + 15.33 \log 321 + 0.39137 \frac{321}{58.08} + 4.33 \times 10^{-3} \frac{321^2}{58.08}$$

$$- 5.627 \times 10^{-6} \frac{321^3}{58.08}$$

$$= 89.43 \text{ J/(mol·K)}$$

$$\Delta H_{vb} = (89.43)(321) = 28,710 \text{ J/mol}$$

$$\text{Error} = \frac{28,710 - 28,280}{28,280} \times 100 = 1.5\%$$

7-14 Enthalpy of Fusion

The enthalpy change on fusion or melting is commonly referred to as the latent heat of fusion. It depends in part on the crystal form of the solid phase, and attempts to obtain general correlations have been unsuccessful. The Clausius-Clapeyron equation is applicable, but its use to calculate ΔH_m requires data on the variation of melting point with pressure, which is seldom available. References for literature values are listed in [83].

Sutra [82] and Mukherjee [66] have indicated how the prediction of ΔH_m might be attained by using the hole theory of liquids, but their calculated values compare poorly with experimental values. Kuczinski [54] presents a theory relating ΔH_m and the modulus of rigidity of the solid.

Good agreement between theoretical and experimental values is shown for eight metallic elements. For monatomic substances, ΔS_m is about equal to the gas constant R [41]. The best theoretical treatment has been presented by Bondi [14], who related the entropy of fusion of molecular crystals to molecular structure.

The difficulty in obtaining a general correlation of ΔH_m in terms of other physical properties is suggested by the selected values tabulated for some hydrocarbons in Table 7-6. It is evident that the simple introduction of a methyl group often has a marked effect; it either increases or decreases ΔH_m. Results for optical and stereoisomers differ markedly. The variation of ΔH_m and the entropy of fusion $\Delta H_m/T_m$ is as great as that of the melting points. None of these are easily correlated with other properties. It appears that there is no simple correlation between ΔH_m and melting point. Table 7-6 shows, for comparison, the relative constancy of the latent heat of vaporization at the normal boiling point. The ratio of $\Delta H_m/\Delta H_{vb}$, however, varies greatly; in the table, values are found between 0.02 and 1.12.

7-15 Enthalpy of Sublimation; Vapor Pressures of Solids

Solids vaporize without melting (sublime) at temperatures below the triple-point temperature. Sublimation is accompanied by an enthalpy increase, or latent heat of sublimation. This may be considered to be the sum of a latent heat of fusion and a hypothetical latent heat of vaporization, even though liquid cannot exist at the pressure and temperature in question.

The latent heat of sublimation ΔH_s is best obtained from solid vapor pressure data. For this purpose, the Clausius-Clapeyron equation (7-2.1) is applicable.

In only a very few cases is the sublimation pressure at the melting point known with accuracy. It can be calculated from a liquid vapor pressure correlation, with input such as T_b and T_c, by extrapolating to the melting point. Such a method is not recommended generally, because none of the vapor pressure correlations are accurate in the very low pressure range. Even if P_{vp} at T_m is known, at least one other value of the vapor pressure of the solid is necessary to calculate ΔH_s from the integrated form of the Clausius-Clapeyron equation. Thus, no useful generalized correlations appear to be available for enthalpies of sublimation for solids.

Another difficulty arises from transitions in the solid phase. Whereas the freezing point is a first-order transition between vapor and solid, the solid may have some liquid-like characteristics such as free rotation. (In a first-order phase transition, there is a discontinuity in volume, enthalpy, and entropy between the phases in equilibrium. Vaporization and melting

are first-order transitions. Second-order transitions are relatively rare and are characterized by the fact that the volume, enthalpy, and entropy are continuous between the phases but there is a discontinuity in the heat capacities and compressibilities between the phases.) In many cases, at temperatures somewhat below the melting point, there is another first-order solid-solid transition between the crystalline-like solid and the more mobile liquid-like solid. The enthalpy of fusion and enthalpy of subli-mation are different for these different solid phases. Ordinarily the liter-ature values for ΔH_m and ΔH_s refer to the solid phase very near its melting point. Bondi [13] suggests that ΔH_m or ΔH_s correlations would be much better if the "most crystalline like" solid phase were considered; i.e., the correlations would be based on the lowest first-order transition tempera-ture, where there is a pronounced semblance of order in the solid struc-ture. Solid-phase transitions are also discussed by Preston et al. [72]. Ref-erences to literature values of ΔH_s are listed in [83].

In some cases it is possible to obtain ΔH_s from thermochemical data by subtracting known values of the enthalpies of formation of solid and vapor. This is hardly a basis for estimation of an unkown ΔH_s, however, since the enthalpies of formation tabulated in the standard references are often based in part on measured values of ΔH_s. If the enthalpies of dis-sociation of both solid and gas phases are known, it is possible to formu-late a cycle including the sublimation of the solid, the dissociation of the vapor, and the recombination of the elements to form the solid compound.

Bondi [13] has suggested an additive-group technique to estimate ΔH_s at the lowest first-order transition temperature for molecular crystals of organic substances and inorganic hydrides, perhalides, and percarbonyls. Usually the lowest first-order transition temperature is not much less than the melting point; e.g., for paraffins the two are almost identical. The exception appears to be n-butane; the usually quoted freezing point is 135 K, whereas the lowest first-order transition temperature is near 107 K. For some other molecules, however, there is a considerable difference. Cyclohexane melts at 279.6 K, but the lowest first-order transition tem-perature is 186 K. There appear to be no general rules for predicting any of the first-order transition temperatures. Bondi's method, however, is only approximate, and great care must be taken in deciding what contri-butions are necessary in many cases.

Finally, as a rough engineering rule, one might estimate ΔH_v and ΔH_m separately and obtain ΔH_s as the sum. The latent heat of fusion is usually less than one-quarter of the sum; therefore, the estimate may be fair even though that for ΔH_m is crude.

If enthalpy-of-fusion information is available, Eq. (7-2.1) may be used to estimate vapor pressures of solids in addition to liquid vapor pressures. The technique, along with its limitations, is illustrated with Example 7-10 [71].

TABLE 7-6 Sample Tabulation of Some Enthalpies and Entropies of Fusion for Simple Hydrocarbons†

	T_m		ΔH_m			$\Delta S_m = \Delta H_m/T$,	ΔH_{vb},	$\dfrac{\Delta H_m}{\Delta H_{vb}}$
	°C	K	J/g	M	J/mol	J/(mol·K)	J/g	
Methane	−182.5	90.7	58.70	16.04	942	10.4	510	0.12
Ethane	−183.3	89.9	95.10	30.07	2,860	31.8	490	0.19
Propane	−187.7	85.5	79.91	44.09	3,523	41.2	427	0.19
n-Butane	−138.4	134.8	80.21	58.12	4,662	34.6	385	0.21
Isobutane	−159.6	113.6	78.12	58.12	4,541	40.0	367	0.21
n-Pentane	−129.7	143.4	116.4	72.15	8,395	58.5	357	0.33
Isopentane	−159.9	113.3	71.38	72.15	5,150	45.5	339	0.21
Neopentane	−16.6	256.6	45.15	72.15	3,257	12.7	315	0.14
n-Hexane	−95.4	177.8	151.2	86.18	13,030	73.3	335	0.45
2-Methylpentane	−153.7	119.5	72.84	86.18	6,278	52.5	323	0.23
2,2-Dimethylbutane	−99.9	173.3	6.74	86.18	581	3.3	305	0.02
2,3-Dimethylbutane	−128.5	144.6	9.41	86.18	811	5.6	317	0.03
n-Heptane	−90.6	182.6	140.0	100.2	14,030	76.8	316	0.44
2-Methylhexane	−118.3	154.9	91.67	100.2	9,185	59.3	306	0.30
3-Ethylpentane	−118.6	154.6	95.31	100.2	9,550	61.8	309	0.31
2,2-Dimethylpentane	−123.8	149.4	58.12	100.2	5,823	39.0	291	0.20
2,4-Dimethylpentane	−119.2	154.0	68.28	100.2	6,842	44.4	295	0.23
3,3-Dimethylpentane	−134.5	138.7	70.54	100.2	7,068	51.0	296	0.24
2,2,3-Trimethylbutane	−24.9	248.3	22.55	100.2	2,260	9.1	289	0.08
n-Octane	−56.8	216.4	181.6	114.2	20,740	95.8	301	0.60
3-Methylheptane	−120.5	152.7	99.62	114.2	11,380	74.5	286	0.33
4-Methylheptane	−120.9	152.2	94.89	114.2	10,840	71.2	297	0.32

n-Nonane	−53.5	219.7	128.3	120.6	15,460	70.4	286	0.42
n-Decane	−29.6	243.5	142.3	201.8	28,720	118.0	276	0.73
n-Dodecane	−9.6	263.6	170.3	216.3	36,830	139.7	256	0.84
n-Octadecane	28.2	301.3	254.5	241.2	61,390	203.7	215	1.12
n-Nonadecane	32	305	268.6	170.6	45,830	150.3	210	0.81
n-Eicosane	36.8	310	282.6	247.3	69,890	225.5	204	1.21
Benzene	5.5	278.7	78.1	125.9	9,833	35.3	394	0.32
Toluene	−95	178	92.1	71.55	6,589	37.0	363	0.20
Ethylbenzene	−94.9	178.2	106.2	86.32	9,167	51.4	339	0.25
o-Xylene	−25.1	248.0	106.2	128.1	13,600	54.8	347	0.37
m-Xylene	−47.9	225.3	106.2	109.0	11,570	51.4	343	0.32
p-Xylene	13.3	286.4	106.2	161	17,100	59.7	340	0.47
n-Propylbenzene	−99.5	173.7	120.2	71.00	8,534	49.1	318	0.22
Isopropylbenzene	−96.0	177.1	120.2	59.20	7,116	40.2	312	0.19
1,2,3-Trimethylbenzene	−25.4	247.7	120.2	69.5	8,350	33.7	333	0.21
1,2,4-Trimethylbenzene	−46	227	120.2	106.9	12,840	56.6	326	0.33
1,3,5-Trimethylbenzene	−44.7	228.4	120.2	80.08	9,626	42.1	325	0.25
Cyclohexane	6.5	279.6	84.2	31.7	2,670	9.5	357	0.09
Methylcyclohexane	−126.5	146.6	98.2	68.6	6,740	46.0	323	0.21
Ethylcyclohexane	−111.3	161.8	112.2	74.18	8,323	51.4	309	0.24
1,1-Dimethylcyclohexane	−33.5	239.7	112.2	5.52	620	2.6	294	0.02
1,cis-2-Dimethylcyclohexane	−50.0	223.1	112.2	14.6	1,640	7.4	305	0.05
1,trans-2-Dimethylcyclohexane	−88.1	185.0	112.2	93.47	10,490	56.7	297	0.31

†Data taken primarily from R. R. Dreisbach, "Physical Properties of Chemical Compounds," *Advan. Chem. Ser., ACS Monogr. 15* and 22, 1955, 1959.

Example 7-10 Use information at the triple point and Eq. (7-2.1) to estimate the vapor pressure of ice at 263 K.

solution Eq. (7-2.1) may be written for the solid in equilibrium with vapor

$$\frac{dP_{vp}^S}{dT} = \frac{\Delta H_{sub}}{T \, \Delta V^S} \tag{i}$$

and for hypothetical subcooled liquid in equilibrium with vapor

$$\frac{dP_{vp}^L}{dT} = \frac{\Delta H_v}{T \, \Delta V^L} \tag{ii}$$

In this example ΔV in both (i) and (ii) may be taken as

$$\Delta V = V^G - V^L \text{ (or } V^S) \simeq V^G = \frac{RT}{P}$$

Subtracting Eq. (i) from (ii), and using $\Delta H_v - \Delta H_{sub} = \Delta H_{fus}$, we get

$$\ln\left(\frac{P_{263}}{P_{273}}\right)^L - \ln\left(\frac{P_{263}}{P_{273}}\right)^S = \int_{273}^{263} \frac{\Delta H_{fus}}{RT^2} dT \tag{iii}$$

ΔH_{fus} is given as a function of temperature by

$$\Delta H_{fus} = (\Delta H_{fus} \text{ at } T_1) + \int_{T_1}^{T} \Delta C_p \, dT \tag{iv}$$

For H_2O, ΔH_{fus} at 273 K is 6008 J/mol; for liquid, $C_p = 75.3$ J/(mol·K); and for ice, $C_p \simeq 37.7$ J/(mol·K).

$$\begin{aligned}\Delta H_{fus} &= 6008 + (37.7)(T - 273) \\ &= 37.7T - 4284\end{aligned} \tag{v}$$

Substitution into (iii) and integration gives

$$\ln\frac{P_{263}^S}{P_{273}^S} - \ln\frac{P_{263}^L}{P_{273}^L} = \frac{37.7}{8.314} \ln\frac{263}{273} + \frac{4284}{8.314}\left(\frac{1}{263} - \frac{1}{273}\right) \tag{vi}$$

$P_{273}^S = P_{273}^L$; P_{263}^L is the vapor pressure of subcooled liquid at 263 K. An extrapolation based on the assumption that $\ln P_{vP}^L$ versus $1/T$ is linear gives $P_{263}^L = 0.00288$ bar. Solving Eq. (vi) gives $P_{263}^S = 0.00261$ bar, which is the same as the literature value.

One should be cautious of the technique used in Example 7-10. Discontinuities can occur in ΔH_{fus} (see Sec. 7-14). Also, the extrapolation of vapor pressures for hypothetical subcooled liquid over large temperature ranges is uncertain (see Sec. 7-6).

Notation

a	parameter in Eqs. (7-4.2) and (7-4.3), constant in Eq. (7-5.2)
A	constant in Eqs. (7-2.3), (7-3.1), (7-6.1), and (7-6.2)
b	parameter in Eq. (7-4.2) and (7-4.4), constant in Eq. (7-5.2)
B	constant in Eqs. (7-2.3) and (7-3.1)
c	constant in Eq. (7-5.2)

C	constant in Eq. (7-3.1)
ΔC_{p_v}	heat capacity of vapor minus heat capacity of liquid, J/(mol·K); see Eq. (7-6.3)
d	constant in Eq. (7-5.2)
$f^{(0)}, f^{(1)}$	functions of reduced temperature in Eq. (7-2.6) and defined in Eqs. (7-2.7) and (7-2.8)
h	parameter defined in Eq. (7-2.5)
ΔH_m	enthalpy change on melting, J/mol
ΔH_v	enthalpy of vaporization, J/mol; ΔH_{v_b} at T_b
ΔH_s	enthalpy of sublimation, J/mol
m	parameter in Eq. (7-4.1)
M	molecular weight
n	exponent in Eq. (7-12.1); usually chosen as 0.38
P	pressure in bars unless stated otherwise; $P_r = P/P_c$
P_c	critical pressure, bars
P_{vp}	vapor pressure; $P_{vp_r} = P_{vp}/P_c$
R	gas constant, 8.314 J/(mol·K)
ΔS_v	entropy of vaporization, J/(mol·K); $\Delta S^{(0)}$ and $\Delta S^{(1)}$, Pitzer parameters in Eq. (7-9.2)
T	temperature, K; $T_r = T/T_c$; T_b, normal boiling point; T_m, melting point; T_c, critical temperature, K
ΔU_v	internal energy of vaporization, J/mol
V	volume, cm³/mol; V_g, saturated vapor; V_L, saturated liqud
V_c	critical volume, cm³/mol
ΔV_v	volume change on vaporization, cm³/mol
X	temperature parameter defined in Eq. (7-12.4)
Z	compressibility factor, PV/RT; Z_g or Z_{SV}, saturated vapor; Z_L or Z_{SL}, saturated liquid
ΔZ_v	$Z_g - Z_L$; ΔZ_{v_b}, at normal boiling point
Z_c	Z at the critical point

GREEK

β	parameter in Eqs. (7-4.1) and (7-10.9)
γ	parameter in Eq. (7-4.1)
Δ^*	quantum gas correction in Eq. (7-4.5)
τ	$1 - T_r$; see Eqs. (7-5.2), (7-9.6), (7-9.7)
ψ	$\Delta H_v/(RT_c \Delta Z_v)$
ω	acentric factor

SUPERSCRIPTS

(0)	simple fluid property
(1)	deviation function
(R1)	property for reference fluid 1
(R2)	property for reference fluid 2

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Fluid Phase Equilibria
in Multicomponent
Systems

8-1 Scope

In the chemical process industries, fluid mixtures are often separated into their components by diffusional operations such as distillation, absorption, and extraction. Design of such separation operations requires quantitative estimates of the partial equilibrium properties of fluid mixtures. Whenever possible, such estimates should be based on reliable experimental data for the particular mixture at conditions of temperature, pressure, and composition corresponding to those of interest. Unfortunately, such data are often not available. In typical cases, only fragmentary data are at hand and it is necessary to reduce and correlate the limited data to make the best possible interpolations and extrapolations. This chapter discusses some techniques that are useful toward that end. Although primary attention is given to nonelectrolytes, a few paragraphs are devoted to aqueous solutions of electrolytes. Emphasis is given to the calculation of fugacities in liquid solutions; fugacities in gaseous mixtures are discussed in Sec. 5-8.

The scientific literature on fluid phase equilibria goes back well over 100 years and has reached monumental proportions, including thousands of articles and hundreds of books and monographs. Table 8-1a and 8-1b give

TABLE 8-1a   Some Useful Books on Fluid-Phase Equilibria

Book	Remarks
Chao, K. C., and R. A. Greenkorn: *Thermodynamics of Fluids,* Dekker, New York, 1975.	Introductory survey including an introduction to statistical thermodynamics of fluids; also gives a summary of surface thermodynamics.
Francis, A. W.: *Liquid-Liquid Equilibrium,* Wiley-Interscience, New York, 1963	Phenomenological discussion of liquid-liquid equilibria with extensive data bibliography.
Hala, E., et al.: *Vapour-Liquid Equilibrium,* 2d English ed., trans. by George Standart, Pergamon, Oxford, 1967.	Comprehensive survey, including a discussion of experimental methods.
Hildebrand, J. H., and R. L. Scott: *Solubility of Nonelectrolytes,* 3d ed., Reinhold, New York, 1950. (Reprinted by Dover, New York, 1964.)	A classic in its field, it gives a survey of solution chemistry from a chemist's point of view. Although out of date, it nevertheless provides physical insight into how molecules "behave" in mixtures.
Hildebrand, J. H., and R. L. Scott: *Regular Solutions,* Prentice Hall, Englewood Cliffs, N.J., 1962.	Updates some of the material in Hildebrand's 1950 book.
Hildebrand, J. H., J. M. Prausnitz, and R. L. Scott: *Regular and Related Solutions,* Van Nostrand Reinhold, New York, 1970.	Further updates some of the material in Hildebrand's earlier books.
King, M. B.: *Phase Equilibrium in Mixtures,* Pergamon, Oxford, 1969.	A general text covering a variety of subjects in mixture thermodynamics.
Modell, M., and R. C. Reid, *Thermodynamics and Its Applications:* 2d ed., Prentice Hall, Englewood Cliffs, N.J., 1983.	This semiadvanced text emphasizes the solution of practical problems through application of fundamental concepts of chemical engineering thermodynamics and discusses surface thermodynamics and systems in potential fields.
Murrell, J. M., and E. A. Boucher: *Properties of Liquids and Solutions,* Wiley, New York, 1982.	A short introduction to the physics and chemistry of the liquid state.
Null, H. R.: *Phase Equilibrium in Process Design,* Wiley-Interscience, New York, 1970.	An engineering-oriented monograph with a variety of numerical examples.
Prausnitz, J. M., R. N. Lichtenthaler, and E. G. Azevedo: *Molecular Thermodynamics of Fluid-Phase Equilibria,* 2d ed., Prentice Hall, Englewood Cliffs, N.J., 1986.	A text which attempts to use molecular-thermodynamic concepts useful for engineering. Written from a chemical engineering point of view.
Prausnitz, J. M., T. F. Anderson, E. A. Grens, C. A. Eckert, R. Hsieh, and J. P. O'Connell: *Computer Calculations for Vapor-Liquid and Liquid Equilibria,* Prentice Hall, Englewood Cliffs, N.J., 1980.	A monograph with detailed computer programs and a (limited) data bank.
Prigogine, I., and R. Defay, *Chemical Thermodynamics,* trans. and rev. by D. H. Everett, Longmans, Green, London, 1954.	A semiadvanced text from a European chemist's point of view. It offers many examples and discusses molecular

Book	Remarks
	principles. Although out of date, it contains much useful information not easily available in standard American texts.
Renon, H., L. Asselineu, G. Cohen, and C. Raimbault, *Calcul sur Ordinateur des Equilibres Liquide-Vapeur et Liquid-Liquid,* Editions Technip, Paris, 1971.	Discusses (in French) the thermodynamic basis for computer calculations for vapor-liquid and liquid-liquid equilibria. Computer programs are given.
Rowlinson, J. S., and F. L. Swinton: *Liquids and Liquid Mixtures,* 3d ed., Butterworth, London, 1982.	Presents a thorough treatment of the physics of fluids and gives some statistical mechanical theories of the equilibrium properties of simple pure liquids and liquid mixtures; contains data bibliography. Primarily for research-oriented readers.
Van Ness, H. C., and M. M. Abbott: *Classical Thermodynamics of Nonelectrolyte Solutions,* McGraw-Hill, New York, 1982.	Systematic, comprehensive, and clear exposition of the principles of classical thermodynamics applied to solutions of nonelectrolytes. Discusses phase equilibria in fluid systems with numerous examples.

TABLE 8-1*b* **Some Useful Books on Fluid Phase Equilibria Data Sources**

Book	Remarks
API Research Project 42: *Properties of Hydrocarbons of High Molecular Weight,* American Petroleum Institute, New York, 1966.	A compilation of physical properties (vapor pressure, liquid density, transport properties) for 321 hydrocarbons with carbon number 11 or more.
API Research Project 44: *Handbook of Vapor Pressures and Heats of Vaporization of Hydrocarbons and Related Compounds,* Thermodynamics Research Center, College Station, Tex., 1971.	A thorough compilation of the vapor pressures and enthalpies of vaporization of alkanes (up to C_{100}), aromatics, and naphthenes (including some with heteroatoms). Other API-44 publications include data on a variety of thermodynamic properties of hydrocarbons and related compounds.
Barton, A. F. M.: *Handbook of Solubility Parameters and other Cohesion Parameters,* CRC Press, Boca Raton, Fla., 1983.	Contains an extensive compilation of data for solubility parameters, cohesive energies, and molar volumes for a variety of substances including polymers. Some correlations (group contributions) are also presented.
Behrens, D., and R. Eckermann: *Chemistry Data Series,* DECHEMA, Frankfurt a.M., Vol. I, *VLE Data Collection,* by J. Gmehling, U. Onken, W. Arlt, P. Grenzheuser, U. Weidlich, and B. Kolbe,	An extensive compilation (in six volumes, some of them consisting of several parts) of thermodynamic property data for pure compounds and mixtures, *PVT* data, heat capacity, enthalpy, and entropy data,

TABLE 8-1*b*   **Some Useful Books on Fluid Phase Equilibria Data Sources** (*Continued*)

Book	Remarks
1977–1984; Vol. II, *Critical Data,* by K. H. Simmrock, 1986; Vol. III, *Heats of Mixing Data Collection,* by C. Christensen, J. Gmehling, P. Rasmussen, and U. Weidlich, 1984; Vol. IV, *Vapor Pressures,* by M. Schönberg and S. Müller, in prep.; Vol. V, *LLE-Data Collection,* by J. M. Sorensen and W. Arlt, 1979–1980; Vol. VI, *VLE for Mixtures of Low Boiling Substances,* by H. Knapp, R. Döring, L. Oellrich, U. Plöcker, and J. M. Prausnitz, 1982.	phase equilibrium data, and transport and interfacial tension data for a variety of inorganic and organic compounds including aqueous mixtures.
Boublik, T., V. Fried, and E. Hala: *The Vapour Pressures of Pure Substances,* 2d ed., Elsevier, Amsterdam, 1984.	Experimental and smoothed data are given for the vapor pressures of pure substances in the normal and low-pressure region; Antoine constants are reported.
Brandrup, J., and E. H. Immergut (eds.): *Polymer Handbook,* 2d ed., Wiley-Interscience, New York, 1975.	A thorough compilation of polymerization reactions and of solution and physical properties of polymers and their associated oligomers and monomers.
Broul, M., J. Nyult, and O. Söhnel: *Solubility in Inorganic Two-Component Systems,* Elsevier, Amsterdam, 1981.	An extensive compilation of data on solubility of inorganic compounds in water.
Christensen, J. J., L. D. Hansen, and R. M. Izatt: *Handbook of Heats of Mixing,* Wiley, New York, 1982.	Experimental heat-of-mixing data for a variety of binary mixtures.
Danner, R. P., and T. E. Daubert (eds.): *Technical Data Book—Petroleum Refining,* American Petroleum Institute, Washington, D.C., 1983.	A two-volume data compilation of the physical, transport, and thermodynamic properties of petroleum fractions and related model compound mixtures of interest to the petroleum-refining industry.
Dymond, J. H., and E. B. Smith: *The Virial Coefficients of Pure Gases and Mixtures,* Oxford, Oxford, 1980.	A critical compilation of data for virial coefficients of pure gases and binary mixtures published to 1979.
Hicks, C. P., K. N. Marsh, A. G. Williamson, I. A. McLure, and C. L. Young: *Bibliography of Thermodynamic Studies,* Chemical Society, London, 1975.	Literature references for vapor-liquid equilibria, enthalpies of mixing, and volume changes of mixing of selected binary systems.
Hirata, M., S. Ohe, and K. Nagahama: *Computer-Aided Data Book of Vapor-Liquid Equilibria,* Elsevier, Amsterdam, 1975.	A compilation of binary experimental data reduced with the Wilson equation and, for high pressures, with a modified Redlich-Kwong equation.
Hiza, M. J., A. J. Kidnay, and R. C. Miller: *Equilibrium Properties of Fluid Mixtures,* 2 vols., IFL/Plenum, New York, 1975, 1982.	Volume 1 contains references for experimental phase equilibria and thermodynamic properties of fluid mixtures of cryogenic interest. Volume 2 updates to January 1980 the references given in Vol. 1. Includes mixtures

Book	Remarks
	containing pentane and some aqueous mixtures.
IUPAC: *Solubility Data Series,* Pergamon, Oxford, 1974.	A multivolume compilation of the solubilities of inorganic gases in pure liquids, liquid mixtures, aqueous solutions, and miscellaneous fluids and fluid mixtures.
Kehiaian, H. V., (ed.-in-chief), and B. J. Kwolinski (exec. officer), *International Data Series: Selected Data on Mixtures,* Thermodynamics Research Center, Chemistry Department, Texas A&M University, College Station, TX 77843, continuing since 1973.	Presents a variety of measured thermodynamic properties of binary mixtures. These properties are often represented by empirical equations.
Van Krevelen, D. W.: *Properties of Polymers,* 2d ed., Elsevier, Amsterdam, 1976.	Presents methods to correlate and predict thermodynamic, transport, and chemical properties of polymers as a function of chemical structure.
Maczynski, A.: *Verified Vapor-Liquid Equilibrium Data,* Polish Scientific Publishers, Warszawa, 1976.	A four-volume compilation of binary vapor-liquid equilibrium data for mixtures of hydrocarbons with a variety of organic compounds; includes many data from the East European literature.
Ohe, S.: *Computer-Aided Data Book of Vapor Pressure,* Data Book Publishing Company, Tokyo, 1976.	Literature references for vapor pressure data for about 2000 substances are given. The data are presented in graphical form, and Antoine constants also are given.
Seidell, A.: *Solubilities of Inorganic and Organic Compounds,* 3d ed., Van Nostrand, New York, 1940 (1941, 1952). Linke, W. L.: *Solubilities of Inorganic and Organic Compounds,* 4th ed., Van Nostrand, Princeton, N.J., 1958 and 1965, vols. 1 and 2.	A two-volume (plus supplement) data compilation. The first volume concerns the solubilities of inorganic and metal organic compounds in single compounds and in mixtures; the second concerns organics; and the supplement updates the solubility references to 1949.
Silcock, H., (ed.): *Solubilities of Inorganic and Organic Compounds,* trans. from Russian, Pergamon, Oxford, 1979.	A systematic compilation of data to 1965 on solubilities of ternary and multicomponent systems of inorganic compounds.
Stephen, H., and T. Stephen (eds): *Solubilities of Inorganic and Organic Compounds.* trans. from Russian, Pergamon, Oxford, 1963.	A five-volume data compilation of solubilities for inorganic, metal-organic and organic compounds in binary, ternary and multicomponent systems.
Tamir, A., E. Tamir, and K. Stephan: *Heats of Phase Change of Pure Components and Mixtures,* Elsevier, Amsterdam, 1983.	An extensive compilation of data published to 1981 on the enthalpy of phase change for pure compounds and mixtures.

TABLE 8-1b   Some Useful Books on Fluid Phase Equilibria Data Sources
(*Continued*)

Book	Remarks
Timmermans, J.: *Physico-chemical Constants of Pure Organic Compounds*, Elsevier, Amsterdam, 1950 and 1965, vols. 1 and 2.	A compilation of data on vapor pressure, density, melting and boiling point, heat-capacity constants, and transport properties of organic compounds (2 vols.).
Constants of Binary Systems, Interscience, New York, 1959.	A four-volume compilation of vapor-liquid and liquid-liquid equilibria, densities of the coexisting phases, transport properties, and enthalpy data for binary concentrated solutions.
Vargaftik, N. B.: *Handbook of Physical Properties of Liquids and Gases: Pure Substances and Mixtures*, 2d ed., Hemisphere, Washington, 1981.	A compilation of thermal, caloric, and transport properties of pure compounds (including organic compounds, SO_2, and halogens) and mainly transport properties of binary gas mixtures, liquid fuels, and oils.
Wichterle, I., J. Linek, and E. Hala: *Vapor-Liquid Equilibrium Data Bibliography*, Elsevier, Amsterdam, 1973 (plus 4 supplements: 1976, 1979, 1982, 1985).	A thorough compilation of literature sources for binary and multicomponent data; includes many references to the East European literature.
Wisniak, J.: *Phase Diagrams*, Elsevier, Amsterdam, 1981.	A literature-source book for published data to 1980 on phase diagrams for a variety of inorganic and organic compounds (2 vols.).
Wisniak, J., and A. Tamir: *Liquid-Liquid Equilibrium and Extraction*, Elsevier, Amsterdam, 1980.	A two-volume literature source book for the equilibrium distribution between two immiscible liquids for data published to 1980.
Wisniak, J., and A. Tamir: *Mixing and Excess Thermodynamic Properties*, Elsevier, Amsterdam, 1978 (supplement 1982).	An extensive bibliographic compilation of data references on mixing and excess properties published between 1900 and 1982.

the authors and titles of some books which are useful for obtaining data and for more detailed discussions. The lists are not exhaustive; they are restricted to publications which are likely to be useful to the practicing engineer in the chemical process industries.

There is an important difference between calculating phase equilibrium compositions and calculating typical volumetric, energetic, or transport properties of fluids of known composition. In the latter case we are interested in the property of the mixture as a whole, whereas in the former we are interested in the *partial* properties of the individual components which constitute the mixture. For example, to find the pressure drop of a liquid mixture flowing through a pipe, we need the viscosity and the density of that liquid mixture at the particular composition of interest. But

if we ask for the composition of the vapor which is in equilibrium with the liquid mixture, it is no longer sufficient to know the properties of the liquid mixture at that particular composition; we must now know, in addition, how certain of its properties (in particular the Gibbs energy) *depend on composition*. In phase equilibrium calculations, we must know *partial* properties, and to find them, we typically differentiate data with respect to composition. Whenever experimental data are differentiated, there is a loss of accuracy, often a serious loss. Since partial, rather than total, properties are needed in phase equilibria, it is not surprising that phase equilibrium calculations are often more difficult and less accurate than those for other properties encountered in chemical process design.

In one chapter it is not possible to present a complete review of a large subject. Also, since this subject is so wide in its range, it is not possible to recommend to the reader simple, unambiguous rules for obtaining quantitative answers to a particular phase equilibrium problem. Since the variety of mixtures is extensive, and since mixture conditions (temperature, pressure, and composition) cover many possibilities, and, finally, since there are large variations in the availability, quantity, and quality of experimental data, the reader cannot escape responsibility for using judgment, which, ultimately, is obtained only by experience.

This chapter, therefore, is qualitatively different from the others in this book. It does not give specific advice on how to calculate specific quantities. It provides only an introduction to some (by no means all) of the tools and techniques which may be useful for an efficient strategy toward calculating particular phase equilibria for a particular process design.

8-2   Thermodynamics of Vapor-Liquid Equilibria

We are concerned with a liquid mixture which, at temperature T and pressure P, is in equilibrium with a vapor mixture at the same temperature and pressure. The quantities of interest are the temperature, the pressure, and the compositions of both phases. Given some of these quantities, our task is to calculate the others.

For every component i in the mixture, the condition of thermodynamic equilibrium is given by

$$f_i^V = f_i^L \tag{8-2.1}$$

where f = fugacity
   V = vapor
   L = liquid

The fundamental problem is to relate these fugacities to mixture composition. In the subsequent discussion, we neglect effects due to surface

forces, gravitation, electric or magnetic fields, semipermeable membranes, or any other special conditions.

The fugacity of a component in a mixture depends on the temperature, pressure, and composition of that mixture. In principle, any measure of composition can be used. For the vapor phase, the composition is nearly always expressed by the mole fraction y. To relate f_i^V to temperature, pressure, and mole fraction, it is useful to introduce the fugacity coefficient ϕ_i

$$\phi_i = \frac{f_i^V}{y_i P} \tag{8-2.2}$$

which can be calculated from vapor phase $PVTy$ data, usually given by an equation of state as discussed in Sec. 5-8. For a mixture of ideal gases $\phi_i = 1$.

The fugacity coefficient ϕ_i depends on temperature and pressure and, in a multicomponent mixture, on *all* mole fractions in the vapor phase, not just y_i. The fugacity coefficient is, by definition, normalized such that as $P \to 0$, $\phi_i \to 1$ for all i. At low pressures, therefore, it is usually a good assumption to set $\phi_i = 1$. But just what "low" means depends on the composition and temperature of the mixture. For typical mixtures of nonpolar (or slightly polar) fluids at a temperature near or above the normal boiling point of the least volatile component, "low" pressure means a pressure less than a few bars. However, for mixtures containing a strongly associating carboxylic acid, e.g., acetic acid–water at 25°C, fugacity coefficients may differ appreciably from unity at pressures much less than 1 bar.† For mixtures containing one component of very low volatility and another of high volatility, e.g., decane-methane at 25°C, the fugacity coefficient of the light component may be close to unity for pressures up to 10 or 20 bar while at the same pressure the fugacity coefficient of the heavy component is typically much less than unity. A detailed discussion is given in chap. 5 of Ref. 97.

The fugacity of component i in the liquid phase is related to the composition of that phase through the activity coefficient γ_i. In principle, any composition scale may be used; the choice is strictly a matter of convenience. For some aqueous solutions, frequently used scales are molality (moles of solute per 1000 g of water) and molarity (moles of solute per liter of solution); for polymer solutions, a useful scale is the volume fraction, discussed briefly in Sec. 8-14. However, for typical solutions containing nonelectrolytes of normal molecular weight (including water), the

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†For moderate pressures, fugacity coefficients can often be estimated with good accuracy as discussed in Ref. 48.

most useful measure of concentration is the mole fraction x. Activity coefficient γ_i is related to x_i and to standard-state fugacity f_i° by

$$\gamma_i \equiv \frac{a_i}{x_i} = \frac{f_i^L}{x_i f_i^\circ} \tag{8-2.3}$$

where a_i is the activity of component i. The standard-state fugacity f_i° is the fugacity of component i at the temperature of the system, i.e., the mixture, and at some arbitrarily chosen pressure and composition. The choice of standard-state pressure and composition is dictated only by convenience, but it is important to bear in mind that the numerical values of γ_i and a_i have no meaning unless f_i° is clearly specified.

While there are some important exceptions, activity coefficients for most typical solutions of nonelectrolytes are based on a standard state where, for every component i, f_i° is the fugacity of *pure* liquid i at system temperature and pressure; i.e., the arbitrarily chosen pressure is the total pressure P, and the arbitrarily chosen composition is $x_i = 1$. Frequently, this standard-state fugacity refers to a hypothetical state, since it may happen that component i cannot physically exist as a pure liquid at system temperature and pressure. Fortunately, for many common mixtures it is possible to calculate this standard-state fugacity by modest extrapolations with respect to pressure; and since liquid phase properties remote from the critical region are not sensitive to pressure (except at high pressures), such extrapolation introduces little uncertainty. In some mixtures, however, namely, those which contain supercritical components, extrapolations with respect to temperature are required, and these, when carried out over an appreciable temperature region, may lead to large uncertainties. We briefly return to this problem in Sec. 8-12.

Whenever the standard-state fugacity is that of the pure liquid at system temperature and pressure, we obtain the limiting relation that $\gamma_i \rightarrow 1$ as $x_i \rightarrow 1$.

8-3 Fugacity of a Pure Liquid

To calculate the fugacity of a pure liquid at a specified temperature and pressure, we require two primary thermodynamic properties: the saturation (vapor) pressure, which depends only on temperature, and the liquid density, which depends primarily on temperature and to a lesser extent on pressure. Unless the pressure is very large, it is the vapor pressure which is by far the more important of these two quantities. In addition, we require volumetric data (equation of state) for pure vapor i at system temperature, but unless the vapor pressure is high or unless there is strong dimerization in the vapor phase, this requirement is of minor, often negligible, importance.

The fugacity of pure liquid i at temperature T and pressure P is given by

$$f_i^L(T, P, x_i = 1) = P_{vpi}(T)\phi_i^s(T) \exp \int_{P_{vpi}}^P \frac{V_i^L(T, P)}{RT} dP \qquad (8\text{-}3.1)$$

where P_{vp} is the vapor pressure (see Chap. 7) and superscript s stands for saturation. The fugacity coefficient ϕ_i^s is calculated from vapor phase volumetric data, as discussed in Sec. 5-8; for typical nonassociated fluids at temperatures well below the critical, ϕ_i^s is close to unity.

The molar liquid volume V_i^L is the ratio of the molecular weight to the density, where the latter is expressed in units of mass per unit volume.† At a temperature well below the critical, a liquid is nearly incompressible. In that case the effect of pressure on liquid phase fugacity is not large unless the pressure is very high or the temperature is very low. The exponential term in Eq. (8-3.1) is called the *Poynting factor*.

To illustrate Eq. (8-3.1), the fugacity of liquid water is shown in Table 8-2. Since ϕ^s for a pure liquid is always less than unity, the fugacity at saturation is always lower than the vapor pressure. However, at pressures well above the saturation pressure, the product of ϕ^s and the Poynting factor may easily exceed unity, and then the fugacity is larger than the vapor pressure.

At 260 and 316°C, the vapor pressure exceeds 40 bar, and therefore pure liquid water cannot exist at these temperatures and 40 bar. Nevertheless, the fugacity can be calculated by a mild extrapolation: in the Poynting factor we neglect the effect of pressure on molar liquid volume.

Table 8-2 indicates that the vapor pressure is the primary quantity in Eq. (8-3.1). When data are not available, the vapor pressure can be estimated, as discussed in Chap. 7. Further, for nonpolar (or weakly polar) liquids, the ratio of fugacity to pressure can be estimated from a generalized (corresponding states) table for liquids, as discussed in Sec. 5-4.

8-4   Simplifications in the Vapor-Liquid Equilibrium Relation

Equation (8-2.1) gives the rigorous, fundamental relation for vapor-liquid equilibrium. Equations (8-2.2), (8-2.3), and (8-3.1) are also rigorous, without any simplifications beyond those indicated in the paragraph following Eq. (8-2.1). Substitution of Eqs. (8-2.2), (8-2.3), and (8-3.1) into Eq. (8-2.1) gives

$$y_i P = \gamma_i x_i P_{vpi} \mathscr{F}_i \qquad (8\text{-}4.1)$$

where $\qquad \mathscr{F}_i = \dfrac{\phi_i^s}{\phi_i} \exp \int_{P_{vpi}}^P \dfrac{V_i^L \, dP}{RT} \qquad (8\text{-}4.2)$

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†For volumetric properties of liquids, see Sec. 3-11.

TABLE 8-2   Fugacity of Liquid Water, bar

Temp., °C	P_{vp}	Fugacity		
		Saturation	41.4 bar	345 bar
37.7	0.06544	0.0654	0.0674	0.0834
149	4.620	4.41	4.50	5.32
260	46.94	39.2	39.2†	45.7
316	106.4	79.9	77.2†	90.6

†Hypothetical because $P < P_{vp}$.

For subcritical components, the correction factor $\mathcal{F}_i$ is often near unity when the total pressure P is sufficiently low. However, even at moderate pressures, we are nevertheless justified in setting $\mathcal{F}_i = 1$ if only approximate results are required and, as happens so often, if experimental information is sketchy, giving large uncertainties in γ.

If, in addition to setting $\mathcal{F}_i = 1$, we assume that $\gamma_i = 1$, Eq. (8-4.1) reduces to the familiar relation known as *Raoult's law*.

In Eq. (8-4.1), γ_i depends on temperature, composition, and pressure. However, remote from critical conditions, and unless the pressure is large, the effect of pressure on γ_i is usually small. [See Eq. (8-12.1).]

8-5   Activity Coefficients; Gibbs-Duhem Equation and Excess Gibbs Energy

In typical mixtures, Raoult's law provides no more than a rough approximation; only when the components in the liquid mixture are similar, e.g., a mixture of n-butane and isobutane, can we assume that γ_i is essentially unity for all components at all compositions. The activity coefficient, therefore, plays a key role in the calculation of vapor-liquid equilibria.

Classical thermodynamics has little to tell us about the activity coefficient; as always, thermodynamics does not give us the experimental quantity we desire but only relates it to other experimental quantities. Thus thermodynamics relates the effect of pressure on the activity coefficient to the partial molar volume, and it relates the effect of temperature on the activity coefficient to the partial molar enthalpy, as discussed in any thermodynamics text (see, for example, chap. 6 of Ref. 97). These relations are of limited use because good data for the partial molar volume and for the partial molar enthalpy are rare.

However, there is one thermodynamic relation which provides a useful tool for correlating and extending limited experimental data: the Gibbs-Duhem equation. This equation is not a panacea, but, given some experimental results, it enables us to use these results efficiently. In essence, the Gibbs-Duhem equation says that, in a mixture, the activity coeffi-

cients of the individual components are not independent of one another but are related by a differential equation. In a binary mixture the Gibbs-Duhem relation is

$$x_1 \left(\frac{\partial \ln \gamma_1}{\partial x_1} \right)_{T,P} = x_2 \left(\frac{\partial \ln \gamma_2}{\partial x_2} \right)_{T,P} \qquad (8\text{-}5.1)\dagger$$

Equation (8-5.1) has several important applications.

1. If we have experimental data for γ_1 as a function of x_1, we can integrate Eq. (8-5.1) and calculate γ_2 as a function of x_2. That is, in a binary mixture, activity coefficient data for one component can be used to predict the activity coefficient of the other component.

2. If we have extensive experimental data for *both* γ_1 and γ_2 as a function of composition, we can test the data for thermodynamic consistency by determining whether or not the data obey Eq. (8-5.1). If the data show serious inconsistencies with Eq. (8-5.1), we may conclude that they are unreliable.

3. If we have limited data for γ_1 and γ_2, we can use an integral form of the Gibbs-Duhem equation; the integrated form provides us with thermodynamically consistent equations which relate γ_1 and γ_2 to x. These equations contain a few adjustable parameters which can be determined from the limited data. It is this application of the Gibbs-Duhem equation which is of particular use to chemical engineers. However, there is no *unique* integrated form of the Gibbs-Duhem equation; many forms are possible. To obtain a particular relation between γ and x, we must assume some model which is consistent with the Gibbs-Duhem equation.

For practical work, the utility of the Gibbs-Duhem equation is best realized through the concept of excess Gibbs energy, i.e., the observed Gibbs energy of a mixture above and beyond what it would be for an ideal solution at the same temperature, pressure, and composition. By definition, an ideal solution is one where all $\gamma_i = 1$. The *total* excess Gibbs energy G^E for a binary solution, containing n_1 moles of component 1 and n_2 moles of component 2, is defined by

$$G^E = RT(n_1 \ln \gamma_1 + n_2 \ln \gamma_2) \qquad (8\text{-}5.2)$$

Equation (8-5.2) gives G^E as a function of *both* γ_1 and γ_2. Upon applying the Gibbs-Duhem equation, we can relate the *individual* activity coefficients γ_1 or γ_2 to G^E by differentiation

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†Note that the derivatives are taken at constant temperature T and constant pressure P. In a binary, two-phase system, however, it is not possible to vary x while holding *both* T and P constant. At ordinary pressures γ is a very weak function of P, and therefore it is often possible to apply Eq. (8-5.1) to isothermal data while neglecting the effect of changing pressure. This subject has been amply discussed in the literature; see, for example, chap. 6 and app. IV in Ref. 97.

$$RT \ln \gamma_1 = \left(\frac{\partial G^E}{\partial n_1}\right)_{T,P,n_2} \tag{8.5.3}$$

$$RT \ln \gamma_2 = \left(\frac{\partial G^E}{\partial n_2}\right)_{T,P,n_1} \tag{8-5.4}$$

Equations (8-5.2) to (8-5.4) are useful because they enable us to interpolate and extrapolate limited data with respect to composition. To do so, we must first adopt some mathematical expression for G^E as a function of composition. Second, we fix the numerical values of the constants in that expression from the limited data; these constants are independent of x, but they usually depend on temperature. Third, we calculate activity coefficients at any desired composition by differentiation, as indicated by Eqs. (8-5.3) and (8-5.4).

To illustrate, consider a simple binary mixture. Suppose that we need activity coefficients for a binary mixture over the entire composition range at a fixed temperature T. However, we have experimental data for only one composition, say $x_1 = x_2 = \frac{1}{2}$. From that one datum we calculate $\gamma_1(x_1 = \frac{1}{2})$ and $\gamma_2(x_2 = \frac{1}{2})$; for simplicity, let us assume symmetrical behavior, that is, $\gamma_1(x_1 = \frac{1}{2}) = \gamma_2(x_2 = \frac{1}{2})$.

We must adopt an expression relating G^E to the composition subject to the conditions that at fixed composition G^E is proportional to $n_1 + n_2$ and that $G^E = 0$ when $x_1 = 0$ or $x_2 = 0$. The simplest expression we can construct is

$$G^E = (n_1 + n_2)g^E = (n_1 + n_2)Ax_1x_2 \tag{8-5.5}$$

where g^E is the excess Gibbs energy per mole of mixture and A is a constant depending on temperature. The mole fraction x is simply related to mole number n by

$$x_1 = \frac{n_1}{n_1 + n_2} \tag{8-5.6}$$

$$x_2 = \frac{n_2}{n_1 + n_2} \tag{8-5.7}$$

The constant A is found from substituting Eq. (8-5.5) into Eq. (8-5.2) and using the experimentally determined γ_1 and γ_2 at the composition midpoint:

$$A = \frac{RT}{(\frac{1}{2})(\frac{1}{2})} [\tfrac{1}{2} \ln \gamma_1(x_1 = \tfrac{1}{2}) + \tfrac{1}{2} \ln \gamma_2(x_2 = \tfrac{1}{2})] \tag{8-5.8}$$

Upon differentiating Eq. (8-5.5) as indicated by Eqs. (8-5.3) and (8-5.4), we find

$$RT \ln \gamma_1 = Ax_2^2 \tag{8-5.9}$$

$$RT \ln \gamma_2 = A x_1^2 \qquad (8\text{-}5.10)$$

With these relations we can now calculate activity coefficients γ_1 and γ_2 at any desired x even though experimental data were obtained only at one point, namely, $x_1 = x_2 = \frac{1}{2}$.

This simplified example illustrates how the concept of excess function, coupled with the Gibbs-Duhem equation, can be used to interpolate or extrapolate experimental data with respect to composition. Unfortunately, the Gibbs-Duhem equation tells nothing about interpolating or extrapolating such data with respect to temperature or pressure.

Equations (8-5.2) to (8-5.4) indicate the intimate relation between activity coefficients and excess Gibbs energy G^E. Many expressions relating g^E (per mole of mixture) to composition have been proposed, and a few are given in Table 8-3. All these expressions contain adjustable constants which, at least in principle, depend on temperature. That dependence may in some cases be neglected, especially if the temperature interval is not large. In practice, the number of adjustable constants per binary is typically two or three; the larger the number of constants, the better the representation of the data but, at the same time, the larger the number of reliable experimental data points required to determine the constants. Extensive and highly accurate experimental data are required to justify more than three empirical constants for a binary mixture at a fixed temperature.†

For many moderately nonideal binary mixtures, all equations for g^E containing two (or more) binary parameters give good results; there is little reason to choose one over another except that the older ones (Margules, van Laar) are mathematically easier to handle than the newer ones (Wilson, NRTL, UNIQUAC). The two-suffix (one-parameter) Margules equation is applicable only to simple mixtures where the components are similar in chemical nature and in molecular size.

For strongly nonideal binary mixtures, e.g., solutions of alcohols with hydrocarbons, the equation of Wilson is probably the most useful because, unlike the NRTL equation, it contains only two adjustable parameters and it is mathematically simpler than the UNIQUAC equation. For such mixtures, the three-suffix Margules equation and the van Laar equation are likely to represent the data with significantly less success, especially in the region dilute with respect to alcohol, where the Wilson equation is particularly suitable.

The four-suffix (three-parameter) Margules equation has no significant advantages over the three-parameter NRTL equation.

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†The models shown in Table 8-3 are not applicable to solutions of electrolytes; such solutions are not considered here. However, brief attention is given to aqueous solutions of volatile weak electrolytes in a later section of this chapter.

Numerous articles in the literature use the Redlich-Kister expansion [see Eq. (8-9.20)] for g^E. This expansion is mathematically identical to the Margules equation.

The Wilson equation is not applicable to a mixture which exhibits a miscibility gap; it is inherently unable, even qualitatively, to account for phase splitting. Nevertheless, Wilson's equation may be useful even for those mixtures where miscibility is incomplete provided attention is confined to the one-phase region.

Unlike Wilson's equation, the NRTL and UNIQUAC equations are applicable to *both* vapor-liquid and liquid-liquid equilibria.† Therefore, mutual solubility data [see Sec. 8-10] can be used to determine NRTL or UNIQUAC parameters but not Wilson parameters. While UNIQUAC is mathematically more complex than NRTL, it has three advantages: (1) it has only two (rather than three) adjustable parameters, (2) UNIQUAC's parameters often have a smaller dependence on temperature, and (3) because the primary concentration variable is a surface fraction (rather than mole fraction), UNIQUAC is applicable to solutions containing small or large molecules, including polymers.

Simplifications: one-parameter equations

It frequently happens that experimental data for a given binary mixture are so fragmentary that it is not possible to determine two (or three) *meaningful* binary parameters; limited data can often yield only one significant binary parameter. In that event, it is tempting to use the two-suffix (one-parameter) Margules equation, but this is usually an unsatisfactory procedure because activity coefficients in a real binary mixture are rarely symmetric with respect to mole fraction. In most cases better results are obtained by choosing the van Laar, Wilson, NRTL, or UNIQUAC equation and reducing the number of adjustable parameters through reasonable physical approximations.

To reduce the van Laar equation to a one-parameter form, for mixtures of nonpolar fluids, the ratio A/B can often be replaced by the ratio of molar liquid volumes: $A/B = V_1^L/V_2^L$. This simplification, however, is not reliable for binary mixtures containing one (or two) polar components.

To simplify the Wilson equation, we first note that

$$\Lambda_{ij} = \frac{V_j^L}{V_i^L} \exp\left(-\frac{\lambda_{ij} - \lambda_{ii}}{RT}\right) \qquad (8\text{-}5.11)$$

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†Wilson [130] has given a three-parameter form of his equation which is applicable also to liquid-liquid equilibria; the molecular significance of the third parameter has been discussed by Renon and Prausnitz [106]. The three-parameter Wilson equation has not received much attention, primarily because it is not readily extended to multicomponent systems.

TABLE 8-3   Some Models for the Excess Gibbs Energy and Subsequent Activity Coefficients for Binary Systems[a]

Name	g^E	Binary parameters	$\ln \gamma_1$ and $\ln \gamma_2$
Two-suffix[b] Margules	$g^E = A x_1 x_2$	A	$RT \ln \gamma_1 = A x_2^2$
			$RT \ln \gamma_2 = A x_1^2$
Three-suffix[b] Margules	$g^E = x_1 x_2 [A + B(x_1 - x_2)]$	A, B	$RT \ln \gamma_1 = (A + 3B)x_2^2 - 4B x_2^3$
			$RT \ln \gamma_2 = (A - 3B)x_1^2 + 4B x_1^3$
van Laar	$g^E = \dfrac{A x_1 x_2}{x_1 (A/B) + x_2}$	A, B	$RT \ln \gamma_1 = A \left(1 + \dfrac{A}{B}\dfrac{x_1}{x_2}\right)^{-2}$
			$RT \ln \gamma_2 = B \left(1 + \dfrac{B}{A}\dfrac{x_2}{x_1}\right)^{-2}$
Wilson	$\dfrac{g^E}{RT} = -x_1 \ln (x_1 + \Lambda_{12} x_2) - x_2 \ln (x_2 + \Lambda_{21} x_1)$	$\Lambda_{12}, \Lambda_{21}$	$\ln \gamma_1 = -\ln (x_1 + \Lambda_{12} x_2) + x_2 \left(\dfrac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \dfrac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2}\right)$
			$\ln \gamma_2 = -\ln (x_2 + \Lambda_{21} x_1) - x_1 \left(\dfrac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \dfrac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2}\right)$
Four-suffix[b] Margules	$g^E = x_1 x_2 [A + B(x_1 - x_2) + C(x_1 - x_2)^2]$	A, B, C	$RT \ln \gamma_1 = (A + 3B + 5C)x_2^2 - 4(B + 4C)x_2^3 + 12C x_2^4$
			$RT \ln \gamma_2 = (A - 3B + 5C)x_1^2 + 4(B - 4C)x_1^3 + 12C x_1^4$

NRTL[c]

$$\frac{g^E}{RT} = x_1 x_2 \left(\frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12} G_{12}}{x_2 + x_1 G_{12}} \right)$$

where $\tau_{12} = \dfrac{\Delta g_{12}}{RT}$ $\tau_{21} = \dfrac{\Delta g_{21}}{RT}$

$\ln G_{12} = -\alpha_{12}\tau_{12}$ $\ln G_{21} = -\alpha_{12}\tau_{21}$

Parameters: $\Delta g_{12},\ \Delta g_{21},\ \alpha_{12}$[d]

$$\ln \gamma_1 = x_2^2 \left[\tau_{21} \left(\frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2} \right]$$

$$\ln \gamma_2 = x_1^2 \left[\tau_{12} \left(\frac{G_{12}}{x_2 + x_1 G_{12}} \right)^2 + \frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2} \right]$$

UNIQUAC[e]

$g^E = g^E(\text{combinatorial}) + g^E(\text{residual})$

$$\frac{g^E(\text{combinatorial})}{RT} = x_1 \ln \frac{\Phi_1}{x_1} + x_2 \ln \frac{\Phi_2}{x_2} + \frac{z}{2}\left(q_1 x_1 \ln \frac{\theta_1}{\Phi_1} + q_2 x_2 \ln \frac{\theta_2}{\Phi_2} \right)$$

$$\frac{g^E(\text{residual})}{RT} = -q_1 x_1 \ln[\theta_1 + \theta_2\tau_{21}] - q_2 x_2 \ln[\theta_2 + \theta_1\tau_{12}]$$

$\Phi_1 = \dfrac{x_1 r_1}{x_1 r_1 + x_2 r_2}$, $\theta_1 = \dfrac{x_1 q_1}{x_1 q_1 + x_2 q_2}$

$\ln \tau_{21} = -\dfrac{\Delta u_{21}}{RT}$ $\ln \tau_{12} = -\dfrac{\Delta u_{12}}{RT}$

Parameters: Δu_{12} and Δu_2

r and q are pure-component parameters and coordination number z = 10

$$\ln \gamma_i = \ln \frac{\Phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\Phi_i} + \Phi_j \left(\ell_i - \frac{r_i}{r_j}\ell_j \right)$$
$$- q_i \ln(\theta_i + \theta_j\tau_{ji}) + \theta_j q_i \left(\frac{\tau_{ji}}{\theta_i + \theta_j\tau_{ji}} - \frac{\tau_{ij}}{\theta_j + \theta_i\tau_{ij}} \right)$$

where $i = 1$ $j = 2$ or $i = 2$ $j = 1$

$\ell_i = \dfrac{z}{2}(r_i - q_i) - (r_i - 1)$

$\ell_j = \dfrac{z}{2}(r_j - q_j) - (r_j - 1)$

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[a] Reference 97 discusses the Margules, van Laar, Wilson, UNIQUAC, and NRTL equations. The UNIQUAC equation is also discussed in Ref. 4.

[b] Two-suffix signifies that the expansion for g^E is quadratic in mole fraction. Three-suffix signifies a third-order, and four-suffix signifies a fourth-order equation.

[c] NRTL = Non Random Two Liquid.

[d] $\Delta g_{12} = g_{12} - g_{22}$; $\Delta g_{21} = g_{21} - g_{11}$.

[e] UNIQUAC = Universal Quasi Chemical. Parameters q and r can be calculated from Eq. (8-10.52).

[f] $\Delta u_{12} = u_{12} - u_{22}$; $\Delta u_{21} = u_{21} - u_{11}$.

where V_i^L is the molar volume of pure liquid i and λ_{ij} is an energy parameter characterizing the interaction of molecule i with molecule j.

The Wilson equation can be reduced to a one-parameter form by assuming that $\lambda_{ij} = \lambda_{ji}$† and that

$$\lambda_{ii} = -\beta(\Delta H_{vi} - RT) \tag{8-5.12}$$

where β is a proportionality factor and ΔH_{vi} is the enthalpy of vaporization of pure component i at T. A similar equation is written for λ_{jj}. When β is fixed, the only adjustable binary parameter is λ_{ij}.

Tassios [118] set $\beta = 1$, but from theoretical considerations it makes more sense to assume that $\beta = 2/z$, where z is the coordination number (typically, $z = 10$). This assumption, used by Wong and Eckert [135] and Schreiber and Eckert [109], gives good estimates for a variety of binary mixtures. Hiranuma and Honma [55] have had some success in correlating λ_{ij} with energy contributions from intermolecular dispersion and dipole-dipole forces.

Ladurelli et al. [65] have suggested the $\beta = 2/z$ for component 2, having the smaller molar volume, while for component 1, having the larger molar volume, $\beta = (2/z)(V_2^L/V_1^L)$. This suggestion follows from the notion that a larger molecule has a larger area of interaction; parameters λ_{ii}, λ_{jj}, and λ_{ij} are considered as interaction energies per segment rather than per molecule. In this particular case the unit segment is that corresponding to one molecule of component 2.

Using similar arguments, Bruin and Prausnitz [23] have shown that it is possible to reduce the number of adjustable binary parameters in the NRTL equation by making a reasonable assumption for α_{12} and by substituting NRTL parameter g_{ii} for Wilson parameter λ_{ii} in Eq. (8-5.12). Bruin gives some correlations for g_{ij}, especially for aqueous systems.

Finally, Abrams and Prausnitz [4] have shown that the UNIQUAC equation can be simplified by assuming that

$$u_{11} = \frac{-\Delta U_1}{q_1} \quad \text{and} \quad u_{22} = \frac{-\Delta U_2}{q_2} \tag{8-5.13}$$

and that

$$u_{12} = u_{21} = (u_{11}u_{22})^{1/2}(1 - c_{12}) \tag{8-5.14}‡$$

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†The simplifying assumption that cross-parameter $\lambda_{ij} = \lambda_{ji}$ (or, similarly, $g_{ij} = g_{ji}$ or $u_{ij} = u_{ji}$) is often useful but is not required by theory unless severe simplifying assumptions concerning liquid structure are made.

‡See preceding footnote.

where, remote from the critical temperature, energy ΔU_i is given very nearly by $\Delta U_i \approx \Delta H_{v_i} - RT$. The only adjustable binary parameter is c_{12}, which, for mixtures of nonpolar liquids, is positive and small compared with unity. For some mixtures containing polar components, however, c_{12} is of the order of 0.5; and when the unlike molecules in a mixture are attracted more strongly than like molecules, c_{12} may be negative, e.g., in acetone-chloroform.

For mixtures of nonpolar liquids, a one-parameter form (van Laar, Wilson, NRTL, UNIQUAC) often gives results nearly as good as those obtained by using two, or even three, parameters. However, if one or both components are polar, significantly better results are usually obtained by using two parameters, provided that the experimental data used to determine the parameters are of sufficient quantity and quality.

8-6 Calculation of Binary Vapor-Liquid Equilibria

First consider the isothermal case. At some constant temperature T, we wish to construct two diagrams; y vs. x and P vs. x. We assume that, since the pressure is low, we can use Eq. (8.4.1) with $\mathscr{F}_i = 1$. The steps toward that end are:

1. Find the pure liquid vapor pressures P_{vp1} and P_{vp2} at T.

2. Suppose a few experimental points for the mixture are available at temperature T. Arbitrarily, to fix ideas, suppose there are five points; i.e., for five values of x there are five corresponding experimental equilibrium values of y and P. For each of these points calculate γ_1 and γ_2 according to

$$\gamma_1 = \frac{y_1 P}{x_1 P_{vp1}} \tag{8-6.1}$$

$$\gamma_2 = \frac{y_2 P}{x_2 P_{vp2}} \tag{8-6.2}$$

3. For each of the five points, calculate the molar excess Gibbs energy g^E:

$$g^E = RT(x_1 \ln \gamma_1 + x_2 \ln \gamma_2) \tag{8-6.3}$$

4. Choose one of the equations for g^E given in Table 8.3. Adjust the constants in that equation to minimize the deviation between g^E calculated from the equation and g^E found from experiment in step 3.

5. Using Eqs. (8-5.3) and (8-5.4), find γ_1 and γ_2 at arbitrarily selected values of x_1 from $x_1 = 0$ to $x_1 = 1$.

6. For each selected x_1 find the corresponding y_1 and P by solving Eqs.

(8-6.1) and (8-6.2) coupled with the mass balance relations $x_2 = 1 - x_1$ and $y_2 = 1 - y_1$. The results obtained give the desired y-vs.-x and P-vs.-x diagrams.

The simple steps outlined above provide a rational, thermodynamically consistent procedure for interpolation and extrapolation with respect to composition. The crucial step is 4. Judgment is required to obtain the best, i.e., the most representative, constants in the expression chosen for g^E. To do so, it is necessary to decide on how to weight the five individual experimental data, some of which may be more reliable than others. For determining the constants, the experimental points which give the most information are those at the ends of the composition scale, that is, y_1 when x_1 is small and y_2 when x_2 is small. Unfortunately, however, these experimental data are often the most difficult to measure. Thus it frequently happens that the data which are potentially most valuable are also the ones which are likely to be least accurate.

Now let us consider the more complicated isobaric case. At some constant pressure P, we wish to construct two diagrams: y vs. x and T vs. x. Assuming that the pressure is low, we again use Eq. (8-4.1) with $\mathscr{F}_i = 1$. The steps toward construction of these diagrams are:

1. Find pure component vapor pressures P_{vp1} and P_{vp2}. Prepare plots (or obtain analytical representation) of P_{vp1} and P_{vp2} vs. temperature in the region where $P_{vp1} \approx P$ and $P_{vp2} \approx P$. (See Chap 7.)

2. Suppose there are available a few experimental data points for the mixture at pressure P or at some other pressure not far removed from P or, perhaps, at some constant temperature such that the total pressure is in the general vicinity of P. As in the previous case, to fix ideas, we arbitrarily set the number of such experimental points at five. By experimental point we mean, as before, that for some value of x_1 we have the corresponding experimental equilibrium values of y_1, T, and total pressure.

For each of the five points, calculate activity coefficients γ_1 and γ_2 according to Eqs. (8-6.1) and (8-6.2). For each point the vapor pressures P_{vp1} and P_{vp2} are evaluated at the experimentally determined temperature for that point. In these equations, the experimentally determined total pressure is used for P; the total pressure measured is not necessarily the same as the pressure for which we wish to construct the equilibrium diagrams.

3. For each of the five points, calculate the molar excess Gibbs energy according to Eq. (8-6.3).

4. Choose one of the equations for g^E given in Table 8-3. As in step 4 of the previous (isothermal) case, find the constants in that equation which give the smallest deviation between calculated values of g^E and those found in step 3. When the experimental data used in Eq. (8-6.3) are isobaric rather than isothermal, it may be advantageous to choose an

expression for g^E which contains the temperature as one of the explicit variables. Such a choice, however, complicates the calculations in step 6.

5. Find γ_1 and γ_2 as functions of x by differentiation according to Eqs. (8-5.3) and (8-5.4).†

6. Select a set of arbitrary values for x_1 for the range $x_1 = 0$ to $x_1 = 1$. For each x_1, by iteration, solve simultaneously the two equations of phase equilibrium [Eqs. (8-6.1) and (8-6.2)] for the two unknowns, y_1 and T. In these equations the total pressure P is now the one for which the equilibrium diagrams are desired.

Simultaneous solution of Eqs. (8-6.1) and (8-6.2) requires trial and error because, at a given x, both y and T are unknown and both P_{vp1} and P_{vp2} are strong, nonlinear functions of T. In addition, γ_1 and γ_2 may also vary with T (as well as x), depending on which expression for g^E has been chosen in step 4. For simultaneous solution of the two equilibrium equations, the best procedure is to assume a reasonable temperature for each selected value of x_1. Using this assumed temperature, calculate y_1 and y_2 from Eqs. (8-6.1) and (8-6.2). Then check if $y_1 + y_2 = 1$. If not, assume a different temperature and repeat the calculation. In this way, for fixed P and for each selected value of x, find corresponding equilibrium values y and T.

Calculation of isothermal or isobaric vapor-liquid equilibria can be efficiently performed with a computer as discussed, for example, in Ref. 99. Further, it is possible in such calculations to include the correction factor $\mathscr{F}_i$ [Eq. (8-4.1)] when necessary. In that event, the calculations are more complex in detail but not in principle.

When the procedures outlined above are followed, the accuracy of any vapor-liquid equilibrium calculation depends primarily on the extent to which the expression for g^E accurately represents the behavior of the mixture at the particular conditions (temperature, pressure, composition) for which the calculation is made. This accuracy of representation often depends not so much on the algebraic form of g^E as on the reliability of the constants appearing in that expression. This reliability, in turn, depends on the quality and quantity of the experimental data used to determine the constants.

Some of the expressions for g^E shown in Table 8-3 have a better theoretical foundation than others, but all have a strong empirical flavor. Experience has indicated that the more recent equations for g^E (Wilson, NRTL, and UNIQUAC) are more consistently reliable than the older equations in the sense that they can usually reproduce accurately even

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†Some error is introduced here because Eqs. (8-5.3) and (8-5.4) are based on the isobaric *and* isothermal Gibbs-Duhem equation. For most practical calculations this error is not serious. See chap. 6 and app. IV of Ref. 97.

highly nonideal behavior by using only two or three adjustable parameters.

The oldest equation of g^E, that of Margules, is a power series in mole fraction. With a power series it is always possible to increase accuracy of representation by including higher terms, where each term is multiplied by an empirically determined coefficient. (The van Laar equation, as shown by Wohl [133], is also a power series in effective volume fraction, but in practice this series is almost always truncated after the quadratic term.) However, inclusion of higher-order terms in g^E is dangerous because subsequent differentiation to find γ_1 and γ_2 can then lead to spurious maxima or minima. Also, inclusion of higher-order terms in binary data reduction often leads to serious difficulties when binary data are used to estimate multicomponent phase equilibria.

It is desirable to use an equation for g^E which is based on a relatively simple model and which contains only two (or at most three) adjustable binary parameters. Experimental data are then used to find the "best" binary parameters. Since experimental data are always of limited accuracy, it often happens that several sets of binary parameters may equally well represent the data within experimental uncertainty [4]. Only in rare cases, when experimental data are both plentiful and highly accurate, is there any justification for using more than three adjustable binary parameters.

8-7 Effect of Temperature on Vapor-Liquid Equilibria

A particularly troublesome question is the effect of temperature on the molar excess Gibbs energy g^E. This question is directly related to s^E, the molar excess entropy of mixing about which little is known.† In practice, either one of two approximations is frequently used.

(a) **Athermal solution.** This approximation sets $g^E = -Ts^E$, which assumes that the components mix at constant temperature without change of enthalpy ($h^E = 0$). This assumption leads to the conclusion that, at constant composition, $\ln \gamma_i$ is independent of T or, its equivalent, that g^E/RT is independent of temperature.

(b) **Regular solution.** This approximation sets $g^E = h^E$, which is the same as assuming that $s^E = 0$. This assumption leads to the conclusion that, at constant composition, $\ln \gamma_i$ varies as $1/T$ or, its equivalent, that g^E is independent of temperature.

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†From thermodynamics, $s^E = -(\partial g^E/\partial T)_{P,x}$ and $g^E = h^E - Ts^E$.

Neither one of these extreme approximations is valid, although the second one is often better than the first. Good experimental data for the effect of temperature on activity coefficients are rare, but when such data are available, they suggest that, for a moderate temperature range, they can be expressed by an empirical equation of the form

$$(\ln \gamma_i)_{\substack{\text{constant} \\ \text{composition}}} = c + \frac{d}{T} \tag{8-7.1}$$

where c and d are empirical constants that depend on composition. In most cases constant d is positive. It is evident that, when $d = 0$, Eq. (8-7.1) reduces to assumption (a) and, when $c = 0$, it reduces to assumption (b). Unfortunately, in typical cases c and d/T are of comparable magnitude.

Thermodynamics relates the effect of temperature on γ_i to the partial molar enthalpy $\overline{h}_i$

$$\left[\frac{\partial \ln \gamma_i}{\partial (1/T)} \right]_{x,P} = \frac{\overline{h}_i - h_i^\circ}{R} \tag{8-7.2}$$

where h_i° is the enthalpy of liquid i in the standard state, usually taken as pure liquid i at system temperature and pressure. Sometimes (but rarely) experimental data for $\overline{h}_i - h_i^\circ$ may be available; if so, they can be used to provide information on how the activity coefficient changes with temperature. However, even if such data are at hand, Eq. (8-7.2) must be used with caution because $\overline{h}_i - h_i^\circ$ depends on temperature and often strongly so.

Some of the expressions for g^E shown in Table 8-3 contain T as an explicit variable. However, one should not therefore conclude that the constants appearing in those expressions are independent of temperature. The explicit temperature dependence indicated provides only an approximation. This approximation is usually, but not always, better than approximation (a) or (b), but, in any case, it is not exact.

Fortunately, the primary effect of temperature on vapor-liquid equilibria is contained in the pure component vapor pressures or, more precisely, in the pure component liquid fugacities [Eq. (8-3.1)]. While the activity coefficients depend on temperature as well as composition, the temperature dependence of the activity coefficient is usually small when compared with the temperature dependence of the pure liquid vapor pressures. In a typical mixture, a rise of 10°C increases the vapor pressures of the pure liquids by a factor of 1.5 or 2, but the change in activity coefficient is likely to be only a few percent, often less than the experimental uncertainty. Therefore, unless there is a large change in temperature, it is frequently satisfactory to neglect the effect of temperature on g^E when calculating vapor-liquid equilibria. However, in calculating liquid-liquid equilibria,

vapor pressures play no role at all, and therefore the effect of temperature on g^E, although small, may seriously affect liquid-liquid equilibria. Even small changes in activity coefficients can have a large effect on multicomponent liquid-liquid equilibria, as briefly discussed in Sec. 8.13.

8-8 Binary Vapor-Liquid Equilibria: Examples

To introduce the general ideas, we present first two particularly simple methods for reduction of vapor-liquid equilibria. These are followed by a brief introduction to more accurate, but also mathematically more complex, procedures.

Example 8-1   Given five experimental vapor-liquid equilibrium data for the binary system methanol (1)–1,2-dichloroethane (2) at 50°C, calculate the P-y-x diagram at 50°C and predict the P-y-x diagram at 60°C.

Experimental Data at 50°C [126]

$100x_1$	$100y_1$	P, bar
30	59.1	0.6450
40	60.2	0.6575
50	61.2	0.6665
70	65.7	0.6685
90	81.4	0.6262

solution   To interpolate in a thermodynamically consistent manner, we must choose an algebraic expression for the molar excess Gibbs energy. For simplicity, we choose the van Laar equation (see Table 8-3). To evaluate the van Laar constants A' and B', we rearrange the van Laar equation in a linear form†

$$\frac{x_1 x_2}{g^E/RT} = D + C(2x_1 - 1) \qquad \text{where} \qquad \begin{aligned} A' &= (D - C)^{-1} \\ B' &= (D + C)^{-1} \end{aligned} \qquad (8\text{-}8.1)$$

Constants D and C are found from a plot of $x_1 x_2 (g^E/RT)^{-1}$ vs. x_1. The intercept at $x_1 = 0$ gives $D - C$, and the intercept at $x_1 = 1$ gives $D + C$. The molar excess Gibbs energy is calculated from the definition

$$\frac{g^E}{RT} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \qquad (8\text{-}8.2)$$

For the five available experimental points, activity coefficients γ_1 and γ_2 are calculated from Eq. (8-4.1) with $\mathcal{F}_i = 1$ and from pure component vapor pressure data.

Table 8-4 gives $x_1 x_2 (g^E/RT)^{-1}$ as needed to obtain van Laar constants. Figure 8-1 shows the linearized van Laar equation. The results shown are obtained with Antoine constants given in Appendix A.

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†From Table 8-3, $A' = A/RT$ and $B' = B/RT$.

TABLE 8-4   Experimental Activity Coefficients for Linearized van Laar Plot, Methanol (1)–1,2-Dichloroethane (2) at 50°C

x_1	γ_1	γ_2	$\dfrac{x_1 x_2}{g^E/RT}$
0.3	2.29	1.21	0.550
0.4	1.78	1.40	0.555
0.5	1.47	1.66	0.560
0.7	1.12	2.46	0.601
0.9	1.02	3.75	0.604

From Fig. 8-1 we obtain the van Laar constants

$$A' = 1.94 \qquad B' = 1.61 \qquad \frac{A'}{B'} = 1.20$$

We can now calculate γ_1 and γ_2 at any mole fraction:

$$\ln \gamma_1 = 1.94 \left(1 + 1.20 \frac{x_1}{x_2} \right)^{-2} \tag{8-8.3}$$

$$\ln \gamma_2 = 1.61 \left(1 + \frac{x_2}{1.20 x_1} \right)^{-2} \tag{8-8.4}$$

By using Eqs. (8-8.3) and (8-8.4) and the pure component vapor pressures, we can now find y_1, y_2, and total pressure P. There are two unknowns: y_1 (or y_2) and P. To find them, we must solve simultaneously the two equations of vapor-liquid equilibrium

$$y_1 = \frac{x_1 \gamma_1 P_{vp1}}{P} \tag{8-8.5}$$

$$1 - y_1 = \frac{x_2 \gamma_2 P_{vp2}}{P} \tag{8-8.6}$$

Calculated results at 50°C are shown in Table 8-5.

To predict vapor-liquid equilibria at 60°C, we assume that the effect of temper-
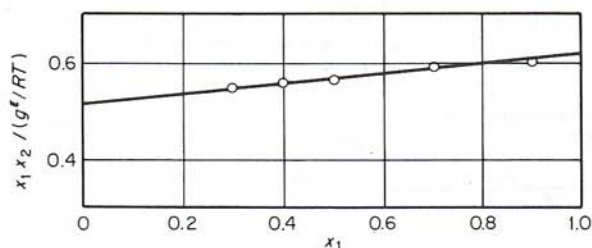
Figure 8-1 Determination of van Laar constants for the system methanol (1)–1,2-dichloroethane (2) at 50°C.

TABLE 8-5 Calculated Vapor-Liquid Equilibria in the System Methanol (1)–1,2-Dichloroethane (2) at 50 and 60°C

$100x_1$	γ_1 50°C	γ_1 60°C	γ_2 50°C	γ_2 60°C	$100y_1$ 50°C	$100y_1$ 60°C	P, bar 50°C	P, bar 60°C	$100\,\Delta y$ 50°C	$100\,\Delta y$ 60°C	$10^3\,\Delta P$, bar 50°C	$10^3\,\Delta P$, bar 60°C
5	5.56	5.28	1.01	1.01	34.1	33.9	0.4528	0.6589				
10	4.53	4.33	1.02	1.02	46.9	46.8	0.5370	0.7830	−0.9	0.4	−1.9	1.5
20	3.15	3.04	1.09	1.09	56.4	56.5	0.6211	0.9102	0.2	0.9	11.1	20.5
40	1.82	1.79	1.37	1.36	61.3	62.1	0.6601	0.9762	1.1	2.2	2.6	26.4
60	1.28	1.27	1.95	1.91	63.8	65.0	0.6693	0.9914	1.3	1.8	−1.7	22.9
80	1.06	1.06	3.01	2.91	71.6	73.1	0.6585	0.9815	0.5	1.2	1.5	34.8
90	1.01	1.01	3.85	3.70	80.9	92.1	0.6249	0.9369	−0.5	−0.1	−1.3	30.3

ature on activity coefficients is given by the regular solution approximation (see Sec. 8-7):

$$\frac{\ln \gamma_i\,(60°C)}{\ln \gamma_i\,(50°C)} = \frac{273 + 50}{273 + 60} \tag{8-8.7}$$

Pure component vapor pressures at 60°C are found from the Antoine relations. The two equations of equilibrium [Eqs. (8-8.5) and (8-8.6)] are again solved simultaneously to obtain y and P as a function of x. Calculated results at 60°C are shown in Table 8-5 and in Fig. 8-2.

Predicted y's are in good agreement with experiment [126], but predicted pressures are too high. This suggests that Eq. (8-8.7) is not a good approximation for this system.

Equation (8-8.7) corresponds to approximation (b) in Sec. 8-7. If approximation (a) had been used, the predicted pressures would have been even higher.
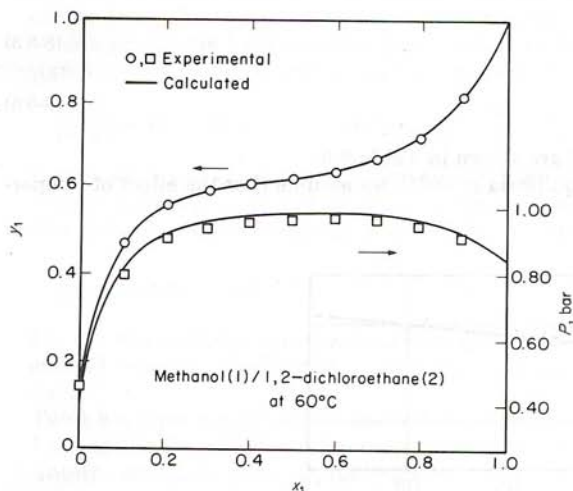
Figure 8-2 Calculated and experimental vapor compositions and total pressures of the system methanol (1)–1,2-dichloroethane (2) at 60°C.

Example 8-2 Given five experimental vapor-liquid equilibrium data for the binary system propanol (1)–water (2) at 1.01 bar, predict the T-y-x diagram for the same system at 1.33 bar.

Experimental Data at 1.01 bar
[82]

$100x_1$	$100y_1$	T, °C
7.5	37.5	89.05
17.9	38.8	87.95
48.2	43.8	87.80
71.2	56.0	89.20
85.0	68.5	91.70

solution To represent the experimental data, we choose the van Laar equation, as in Example 8-1. Since the temperature range is small, we neglect the effect of temperature on the van Laar constants.

As in Example 8-1, we linearize the van Laar equation as shown in Eq. (8-8.1). To obtain the van Laar constants A' and B', we need, in addition to the data shown above, vapor pressure data for the pure components.

Activity coefficients γ_1 and γ_2 are calculated from Eq. (8-4.1) with $\mathcal{F}_i = 1$, and g^E/RT is calculated from Eq. (8-8.2). Antoine constants are from Appendix A. Results are given in Table 8-6. The linearized van Laar plot is shown in Fig. 8-3. From the intercepts in Fig. 8-3 we obtain

$$A' = 2.60 \qquad B' = 1.13 \qquad \frac{A'}{B'} = 2.30 \tag{8-8.8}$$

Activity coefficients γ_1 and γ_2 are now given by the van Laar equations

$$\ln \gamma_1 = 2.60 \left(1 + 2.30\frac{x_1}{x_2} \right)^{-2} \tag{8-8.9}$$

$$\ln \gamma_2 = 1.13 \left(1 + \frac{x_2}{2.30x_1} \right)^{-2} \tag{8-8.10}$$

TABLE 8-6 **Experimental Activity Coefficients for Linearized van Laar Plot, n-Propanol (1)–Water (2) at 1.01 Bar**

$100x_1$	T, °C	γ_1	γ_2	$\dfrac{x_1x_2}{g^E/RT}$
7.5	89.05	6.84	1.01	0.446
17.9	87.95	3.10	1.17	0.448
48.2	87.80	1.31	1.71	0.615
71.2	89.20	1.07	2.28	0.720
85.0	91.70	0.99	2.85	0.848
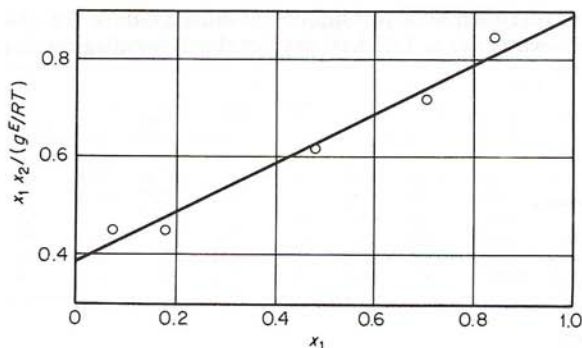
Figure 8-3 Determination of van Laar constants for the system n-propanol (1)–water at 1.01 bar.

To obtain the vapor-liquid equilibrium diagram at 1.33 bar, we must solve simultaneously the two equations of equilibrium

$$y_1 = \frac{\gamma_1 x_1 P_{vp1}(T)}{1.33} \tag{8-8.11}$$

$$1 - y_1 = y_2 = \frac{\gamma_2 x_2 P_{vp2}(T)}{1.33} \tag{8-8.12}$$

In this calculation we assume that γ_1 and γ_2 depend only on x (as given by the van Laar equations) and not on temperature. However, P_{vp1} and P_{vp2} are strong functions of temperature.

The two unknowns in the equations of equilibrium are y_1 and T. To solve for these unknowns, it is also necessary to use the Antoine relations for the two pure components.

The required calculations contain the temperature as an implicit variable; solution of the equations of equilibrium must be by iteration.

While iterative calculations are best performed with a computer, in this example it is possible to obtain results rapidly by hand calculations. Dividing one of the equations of equilibrium by the other, we obtain

$$y_1 = \left(1 + \frac{\gamma_2 x_2}{\gamma_1 x_1} \frac{P_{vp2}}{P_{vp1}}\right)^{-1} \tag{8-8.13}$$

Although P_{vp2} and P_{vp1} are strong functions of temperature, the ratio P_{vp2}/P_{vp1} is a much weaker function of temperature.

For a given x_1, find γ_2/γ_1 from the van Laar equations. Choose a reasonable temperature and find P_{vp2}/P_{vp1} from the Antoine relations. Equation (8-8.13) then gives a first estimate for y_1. Using this estimate, find P_{vp1} from

$$P_{vp1} = \frac{1.33 y_1}{x_1 \gamma_1} \tag{8-8.14}$$

The Antoine relation for component 1 then gives a first estimate for T. By using this T, find the ratio P_{vp2}/P_{vp1} and, again using Eq. (8-8.13), find the second estimate for y_1. This second estimate for y_1 is then used with the Antoine relation to find the second estimate for T. Repeat until there is negligible change in the estimate for T.

It is clear that Eq. (8-8.14) for component 1 could be replaced with the analogous equation for component 2. Which one should be used? In principle, either one

TABLE 8-7   Calculated Vapor-Liquid Equilibria for
***n*-Propanol (1)–Water (2) at 1.33 Bar**

$100x_1$	γ_1	γ_2	$T, °C$	$100y_1$
5	7.92	1.01	98.4	31.6
10	5.20	1.05	96.0	37.9
20	2.85	1.16	95.3	40.5
40	1.50	1.51	95.0	42.2
50	1.27	1.73	95.2	44.9
60	1.14	1.98	95.5	48.8
80	1.02	2.51	98.2	64.6
90	1.01	2.79	100.6	78.5

may be used, but for components of comparable volatility, convergence is likely to be more rapid if Eq. (8-8.14) is used for $x_1 > \frac{1}{2}$ and the analogous equation for component 2 is used when $x_1 < \frac{1}{2}$. However, if one component is much more volatile than the other, the equation for that component is likely to be more useful. Table 8-7 presents calculated results at 1.33 bar. Unfortunately, no experimental results at this pressure are available for comparison.

The two simple examples above illustrate the essential steps for calculating vapor-liquid equilibria from limited experimental data. Because of their illustrative nature, these examples are intentionally simplified, and for more accurate results it is desirable to replace some of the details by more sophisticated techniques. For example, it may be worthwhile to include corrections for vapor phase nonideality and perhaps the Poynting factor, i.e., to relax the simplifying assumption $\mathscr{F}_i = 1$ in Eq. (8-4.1). At the modest pressures encountered here, however, such modifications are likely to have a small effect. A more important change would be to replace the van Laar equation with a better equation for the activity coefficients, e.g., the Wilson equation or the UNIQUAC equation. If this is done, the calculational procedure is the same but the details of computation are more complex. Because of algebraic simplicity, the van Laar equations can easily be linearized, and therefore a convenient graphical procedure can be used to find the van Laar constants.† An equation like UNIQUAC or that of Wilson cannot easily be linearized, and therefore, for practical application, it is necessary to use a computer for data reduction to find the binary constants which appear in the equation.

In Examples 8-1 and 8-2 we have not only made simplifications in the thermodynamic relations but have also neglected to take into quantitative consideration the effect of experimental error.

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†The three-suffix Margules equation is also easily linearized, as shown by H. C. Van Ness, "Classical Thermodynamics of Nonelectrolyte Solutions," p. 129, Pergamon, New York, 1964.

It is beyond the scope of this chapter to discuss in detail the highly sophisticated statistical methods now available for optimum reduction of vapor-liquid equilibrium data. Nevertheless, a very short discussion may be useful as an introduction for readers who want to obtain the highest possible accuracy from the available data.

A particularly effective data reduction method is described by Fabries and Renon [33] and by Anderson, Abrams, and Grens [7], who base their analysis on the principle of maximum likelihood while taking into account probable experimental errors in all experimentally determined quantities.

To illustrate the general ideas, we define a calculated pressure (constraining function) by

$$P^c = \exp\left(x_1 \ln \frac{\gamma_1 x_1 f^L_{\text{pure 1}}}{y_1 \phi_1} + x_2 \ln \frac{\gamma_2 x_2 f^L_{\text{pure 2}}}{y_2 \phi_2}\right) \tag{8-8.15}$$

where $f^L_{\text{pure } i}$ is at system temperature and pressure. The most probable values of the parameters (appearing in the function chosen for g^E) are those which minimize the function I:

$$I = \sum_i \left(\frac{(x_i^0 - x_i^M)^2}{\sigma_{xi}^2} + \frac{(y_i^0 - y_i^M)^2}{\sigma_{yi}^2} + \frac{(P_i^0 - P_i^M)^2}{\sigma_{Pi}^2} + \frac{(T_i^0 - T_i^M)^2}{\sigma_{Ti}^2}\right) \tag{8-8.16}$$

Superscript M indicates a measured value, and superscript 0 indicates an estimate of the true value of the variable. The σ^2's are estimates of the variances of the measured values, i.e., an indication of the probable experimental uncertainty. These may vary from one point to another but need not.

By using experimental P-T-x-y data and the UNIQUAC equation with estimated parameters $u_{12} - u_{22}$ and $u_{21} - u_{11}$, we obtain estimates of x_i^0, y_i^0, T_i^0, and P_i^0. The last of these is found from Eq. (8-8.15). We then evaluate I, having previously set average variances σ_x^2, σ_y^2, σ_P^2, and σ_T^2 from a critical inspection of the data's quality. Upon changing the estimate of UNIQUAC parameters, we calculate a new I; with a suitable computer program, we search for the parameters which minimize I. Convergence is achieved when, from one iteration to the next, the relative change in I is less than 10^{-5}. After the last iteration, the variance of fit σ_F^2 is given by

$$\sigma_F^2 = \frac{I}{D - L} \tag{8-8.17}$$

where D is the number of data points and L is the number of adjustable parameters.

Since all experimental data have some experimental uncertainty, and since any equation for g^E can provide only an approximation to the experimental results, it follows that the parameters obtained from data reduction are not unique; there are many sets of parameters which can equally
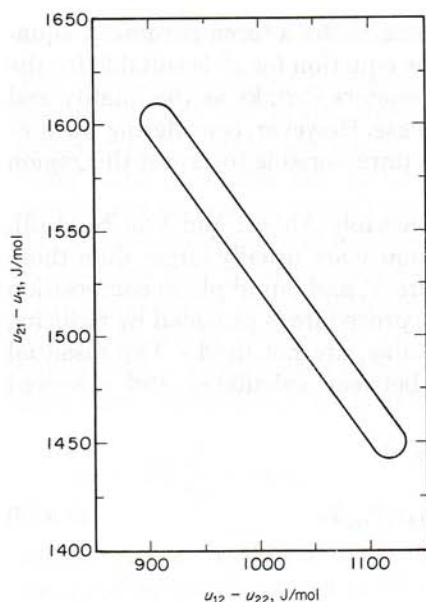
Figure 8-4 The 99 percent confidence ellipse for UNIQUAC parameters in the system ethanol (1)–water (2) at 70°C.

well represent the experimental data within experimental uncertainty. To illustrate this lack of uniqueness, Fig. 8-4 shows results of data reduction for the binary mixture ethanol (1)–water at 70°C. Experimental data reported by Mertl [76] were reduced by using the UNIQUAC equation with the variances

$$\sigma_x = 10^{-3} \qquad \sigma_y = 10^{-2} \qquad \sigma_p = 6.7 \times 10^{-4}\,\text{bar} \qquad \sigma_T = 0.1\,\text{K}$$

For this binary system, the fit is very good; $\sigma_F^2 = 5 \times 10^{-4}$.

The ellipse in Fig. 8-4 clearly shows that, although parameter $u_{21} - u_{11}$ is strongly correlated with parameter $u_{12} - u_{22}$, there are many sets of these parameters that can equally well represent the data. The experimental data used in data reduction are not sufficient to fix a unique set of "best" parameters. Realistic data reduction can determine only a region of parameters.†

While Fig. 8-4 pertains to the UNIQUAC equation, similar results are obtained when other equations for g^E are used; only a region of acceptable parameters can be obtained from $P\text{-}T\text{-}y\text{-}x$ data. For a two-parameter

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†Instead of the restraint given by Eq. (8-8.15), it is sometimes preferable to use instead two restraints; first, Eq. (8-8.18), and second,

$$y_1 = \frac{x_1\gamma_1 f_1^0/\phi_1}{x_1\gamma_1 f_1^0/\phi_1 + x_2\gamma_2 f_2^0/\phi_2}$$

or the corresponding equation for y_2.

equation this region is represented by an area; for a three-parameter equation it is represented by a volume. If the equation for g^E is suitable for the mixture, the region of acceptable parameters shrinks as the quality and quantity of the experimental data increase. However, considering the limits of both theory and experiment, it is unreasonable to expect this region to shrink to a single point.

As indicated by numerous authors, notably Abbott and Van Ness [3], experimental errors in vapor composition y are usually larger than those in experimental pressure P, temperature T, and liquid phase composition x. Therefore, a relatively simple fitting procedure is provided by reducing only P-x-T data; y data, even if available, are not used.† The essential point is to minimize the deviation between calculated and observed pressures.

The pressure is calculated according to

$$P_{\text{calc}} = y_1 P + y_2 P = \gamma_1 x_1 P_{\text{vp1}} \mathscr{F}_1 + \gamma_2 x_2 P_{\text{vp2}} \mathscr{F}_2 \tag{8-8.18}$$

where $\mathscr{F}_i$ is given by Eq. (8-4.2).

Thermodynamically consistent equations are now chosen to represent γ_1 and γ_2 as functions of x (and perhaps T); some are suggested in Table 8-3. These equations contain a number of adjustable binary parameters. With a computer, these parameters can be found by minimizing the deviation between calculated and measured pressures.

At low pressures, we can assume that $\mathscr{F}_1 = \mathscr{F}_2 = 1$. However, at higher pressures, correction factors $\mathscr{F}_1$ and $\mathscr{F}_2$ are functions of pressure, temperature, and vapor compositions y_1 and y_2; these compositions are calculated from

$$y_1 = \frac{\gamma_1 x_1 P_{\text{vp1}} \mathscr{F}_1(P, T, y)}{P} \quad \text{and} \quad y_2 = \frac{\gamma_2 x_2 P_{\text{vp2}} \mathscr{F}_2(P, T, y)}{P} \tag{8-8.19}‡$$

The data reduction scheme, then, is iterative; to get started, it is necessary first to assume an estimated y for each x. After the first iteration, a new set of estimated y's is found from Eq. (8-8.19). Convergence is achieved when, following a given iteration, the y's calculated differ negligibly from those calculated after the previous iteration and when the pressure deviation is minimized.

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†This technique is commonly referred to as *Barker's method*.

‡If the Lewis fugacity rule is used to calculate vapor phase fugacity coefficients, $\mathscr{F}_1$ and $\mathscr{F}_2$ depend on pressure and temperature but are independent of y. The Lewis rule provides mathematical simplification, but, unfortunately, it is a poor rule. If a computer is available, there is no need to use it.

8-9   Multicomponent Vapor-Liquid Equilibria

The equations required to calculate vapor-liquid equilibria in multicomponent systems are, in principle, the same as those required for binary systems. In a system containing N components, we must solve N equations simultaneously: Eq. (8-4.1) for each of the N components. We require the saturation (vapor) pressure of each component, as a pure liquid, at the temperature of interest. If all pure component vapor pressures are low, the total pressure also is low. In that event, the factor $\mathcal{F}_i$ [Eq. (8-4.2)] can often be set equal to unity.

Activity coefficients γ_i are found from an expression for the excess Gibbs energy, as discussed in Sec. (8-5). For a mixture of N components, the excess Gibbs energy G^E is defined by

$$G^E = RT \sum_{i=1}^{N} n_i \ln \gamma_i \qquad (8\text{-}9.1)$$

where n_i is the number of moles of component i. The molar excess Gibbs energy g^E is simply related to G^E by

$$g^E = \frac{G^E}{n_T} \qquad (8\text{-}9.2)$$

where n_T, the total number of moles, is equal to $\sum_{i=1}^{N} n_i$.

Individual activity coefficients can be obtained from G^E upon introducing the Gibbs-Duhem equation for a multicomponent system at constant temperature and pressure. That equation is

$$\sum_{i=1}^{N} n_i \, d \ln \gamma_i = 0 \qquad (8\text{-}9.3)$$

The activity coefficient γ_i is found by a generalization of Eq. (8-5.3):

$$RT \ln \gamma_i = \left(\frac{\partial G^E}{\partial n_i} \right)_{T,P,n_j} \qquad (8\text{-}9.4)$$

where n_j indicates that all mole numbers (except n_i) are held constant in the differentiation.

The key problem in calculating multicomponent vapor-liquid equilibria is to find an expression for g^E which provides a good approximation for the properties of the mixture. Toward that end, the expressions for g^E for binary systems, shown in Table 8-3, can be extended to multicomponent systems. A few of these are shown in Table 8-8.

TABLE 8-8 Three Expressions for the Molar Excess Gibbs Energy and Activity Coefficients of Multicomponent Systems Using Only Pure Component and Binary Parameters
Symbols defined in Table 8-3; the number of components is N

Name	Molar excess Gibbs energy	Activity coefficient for component i
Wilson	$\dfrac{g^E}{RT} = -\sum_i^N x_i \ln\left(\sum_j^N x_j\Lambda_{ij}\right)$	$\ln\gamma_i = -\ln\left(\sum_j^N x_j\Lambda_{ij}\right) + 1 - \sum_k^N \dfrac{x_k\Lambda_{ki}}{\sum_j^N x_j\Lambda_{kj}}$
NRTL	$\dfrac{g^E}{RT} = \sum_i^N x_i \dfrac{\sum_j^N \tau_{ji}G_{ji}x_j}{\sum_k^N G_{ki}x_k}$	$\ln\gamma_i = \dfrac{\sum_j^N \tau_{ji}G_{ji}x_j}{\sum_k^N G_{ki}x_k} + \sum_j^N \dfrac{x_jG_{ij}}{\sum_k^N G_{kj}x_k}\left(\tau_{ij} - \dfrac{\sum_k^N x_k\tau_{kj}G_{kj}}{\sum_k^N G_{kj}x_k}\right)$
UNIQUAC†	$\dfrac{g^E}{RT} = \sum_i^N x_i \ln\dfrac{\Phi_i}{x_i} + \dfrac{z}{2}\sum_i^N q_i x_i \ln\dfrac{\theta_i}{\Phi_i}$ $\qquad - \sum_i^N q_i x_i \ln\left(\sum_j^N \theta_j\tau_{ji}\right)$	$\ln\gamma_i = \ln\dfrac{\Phi_i}{x_i} + \dfrac{z}{2}q_i\ln\dfrac{\theta_i}{\Phi_i} + l_i$ $\qquad - \dfrac{\Phi_i}{x_i}\sum_j^N x_j l_j - q_i \ln\left(\sum_j^N \theta_j\tau_{ji}\right) + q_i$ $\qquad - q_i\sum_j^N \dfrac{\theta_j\tau_{ij}}{\sum_k^N \theta_k\tau_{kj}}$

where

$$\Phi_i = \frac{r_i x_i}{\sum_k^N r_k x_k} \qquad \text{and} \qquad \theta_i = \frac{q_i x_i}{\sum_k^N q_k x_k}$$

†Parameters q and r can be calculated from Eq. (8-10.52).

The excess Gibbs energy concept is particularly useful for multicomponent mixtures because in many cases, to a good approximation, extension from binary to multicomponent systems can be made in such a way that only binary parameters appear in the final expression for g^E. When that is the case, a large saving in experimental effort is achieved, since experimental data are then required only for the mixture's constituent binaries, not for the multicomponent mixture itself. For example, activity coefficients in a ternary mixture (components 1, 2, and 3) can often be calculated with good accuracy by using only experimental data for the three binary mixtures: components 1 and 2, components 1 and 3, and components 2 and 3.

Many physical models for g^E for a binary system consider only two-body intermolecular interactions, i.e., interactions between two (but not more) molecules. Because of the short range of molecular interaction between nonelectrolytes, it is often permissible to consider only interactions between molecules that are first neighbors and then to sum all the two-body, first-neighbor interactions. A useful consequence of these simplifying assumptions is that extension to ternary (and higher) systems requires only binary, i.e., two-body, information; no ternary (or higher) constants appear. However, not all physical models use this simplifying assumption, and those which do not often require additional simplifying assumptions if the final expression for g^E is to contain only constants derived from binary data.

To illustrate with the simplest case, consider the two-suffix Margules relation for g^E (Table 8-3). For a binary mixture, this relation is given by Eq. (8-5.5), leading to activity coefficients given by Eqs. (8-5.9) and (8-5.10). The generalization to a system containing N components is

$$g^E = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} A_{ij} x_i x_j \tag{8-9.5}$$

where the factor $\frac{1}{2}$ is needed to avoid counting molecular pairs twice. The coefficient A_{ij} is obtained from data for the ij binary. [In the summation indicated in Eq. (8-9.5), $A_{ii} = A_{jj} = 0$ and $A_{ij} = A_{ji}$.] For a ternary system Eq. (8-9.5) becomes

$$g^E = A_{12} x_1 x_2 + A_{13} x_1 x_3 + A_{23} x_2 x_3 \tag{8-9.6}$$

Activity coefficients are obtained by differentiating Eq. (8-9.6) according to Eq. (8-9.4), remembering that $x_i = n_i/n_T$, where n_T is the total number of moles. Upon performing this differentiation, we obtain for component k

$$RT \ln \gamma_k = \sum_{i=1}^{N} \sum_{j=1}^{N} (A_{ik} - \tfrac{1}{2} A_{ij}) x_i x_j \tag{8-9.7}$$

For a ternary system, Eq. (8-9.7) becomes

$$RT \ln \gamma_1 = A_{12}x_2^2 + A_{13}x_3^2 + (A_{12} + A_{13} - A_{23})x_2x_3 \qquad (8\text{-}9.8)$$

$$RT \ln \gamma_2 = A_{12}x_1^2 + A_{23}x_3^2 + (A_{12} + A_{23} - A_{13})x_1x_3 \qquad (8\text{-}9.9)$$

$$RT \ln \gamma_3 = A_{13}x_1^2 + A_{23}x_2^2 + (A_{13} + A_{23} - A_{12})x_1x_2 \qquad (8.9.10)$$

All constants appearing in these equations can be obtained from binary data; no ternary data are required.

Equations (8-9.8) to (8-9.10) follow from the simplest model for g^E. This model is adequate only for nearly ideal mixtures, where the molecules of the constituent components are similar in size and chemical nature, e.g., benzene-cyclohexane-toluene. For most mixtures encountered in the chemical process industries, more elaborate models for g^E are required.

First it is necessary to choose a model for g^E. Depending on the model chosen, some (or possibly all) of the constants in the model may be obtained from binary data. Second, individual activity coefficients are found by differentiation, as indicated in Eq. (8-9.4).

Once we have an expression for the activity coefficients as functions of liquid phase composition and temperature, we can then obtain vapor-liquid equilibria by solving simultaneously *all* the equations of equilibrium. For every component i in the mixture,

$$y_iP = \gamma_ix_iP_{vpi}\mathscr{F}_i \qquad (8\text{-}9.11)$$

where $\mathscr{F}_i$ is given by Eq. (8-4.2).

Since the equations of equilibrium are highly nonlinear, simultaneous solution is almost always achieved only by iteration. Such iterations can be efficiently performed with a computer [99].

Example 8-3   A simple example illustrating how binary data can be used to predict ternary equilibria is provided by Steele, Poling, and Manley [116], who studied the system 1-butene (1)–isobutane (2)–1,3-butadiene (3) in the range 4.4 to 71°C.

solution   Steele et al. measured isothermal total pressures of the three binary systems as functions of liquid composition. For the three pure components, the pressures are given as functions of temperature by the Antoine equation

$$\ln P_{vp} = a + b(c + t)^{-1} \qquad (8\text{-}9.12)$$

where P_{vp} is in bars and t is in degrees Celsius. Pure component constants a, b, and c are shown in Table 8-9.

For each binary system the total pressure P is given by

$$P = \sum_{i=1}^{2} y_iP = \sum_{i=1}^{2} x_i\gamma_iP_{vpi} \exp\frac{(V_i^l - B_{ii})(P - P_{vpi})}{RT} \qquad (8\text{-}9.13)$$

where γ_i is the activity coefficient of component i in the liquid mixture, V_i^l is the molar volume of pure liquid i, and B_{ii} is the second virial coefficient of pure vapor

TABLE 8-9 Antoine Constants for 1-Butene (1)–Isobutene (2)–1,3-Butadiene (3) at 4.4 to 71°C [Eq. (8-9.12)] [116]

Component	a	$-b$	c
(1)	9.37579	2259.58	247.658
(2)	9.47209	2316.92	256.961
(3)	9.43739	2292.47	247.799

i, all at system temperature T. Equation (8-9.13) assumes that vapor phase imperfections are described by the (volume explicit) virial equation truncated after the second term (see Sec. 3-5). Also, since the components are chemically similar, and since there is little difference in molecular size, Steele et al. used the Lewis fugacity rule $B_{ij} = (\frac{1}{2})(B_{ii} + B_{jj})$. For each pure component, the quantity $(V_i^L - B_{ii})/RT$ is shown in Table 8-10.

For the molar excess Gibbs energy of the binary liquid phase, a one-parameter (two-suffix) Margules equation was assumed:

$$\frac{g_{ij}^E}{RT} = A'_{ij} x_i x_j \tag{8-9.14}$$

From Eq. (8-9.14) we have

$$\ln \gamma_i = A'_{ij} x_j^2 \quad \text{and} \quad \ln \gamma_j = A'_{ij} x_i^2 \tag{8-9.15}$$

Equation (8-9.15) is used at each temperature to reduce the binary, total-pressure data yielding the Margules constant A'_{ij}. For the three binaries studied, Margules constants are shown in Table 8-11.

To predict ternary phase equilibria, Steele et al. assume that the molar excess Gibbs energy is given by

$$\frac{g^E}{RT} = A'_{12} x_1 x_2 + A'_{13} x_1 x_3 + A'_{23} x_2 x_3 \tag{8-9.16}$$

Activity coefficients γ_1, γ_2, and γ_3 are then found by differentiation. [See Eqs. (8-9.8) to (8-9.10), noting that $A'_{ij} = A_{ij}/RT$.]

Vapor-liquid equilibria are found by writing for each component

$$y_i P = \gamma_i x_i P_{vpi} \mathcal{F}_i \tag{8-9.17}$$

TABLE 8-10 Pure Component Parameters for 1-Butene (1)–Isobutane (2)–1,3-Butadiene (3) [116]

Temperature, °C	$10^3 (V_i^L - B_{ii})/RT$, bar^{-1}		
	(1)	(2)	(3)
4.4	35.13	38.62	33.92
21	33.04	33.04	31.85
38	28.30	28.82	27.60
54	24.35	25.02	23.32
71	21.25	22.12	20.33

TABLE 8-11   Margules Constants A'_{ij}
for Three Binary Mixtures formed by
1-Butene (1), Isobutane (2), and 1,3-
Butadiene (3) [116]

Temp. °C	$10^3 A'_{12}$	$10^3 A'_{13}$	$10^3 A'_{23}$
4.4	73.6	77.2	281
21	60.6	64.4	237
38	52.1	54.8	201
54	45.5	47.6	172
71	40.7	42.4	147

where, consistent with earlier assumptions,

$$\mathcal{F}_i = \exp\frac{(V_i^L - B_{ii})(P - P_{\text{vp}i})}{RT} \tag{8-9.18}$$

Steele and coworkers find that predicted ternary vapor-liquid equilibria are in excellent agreement with their ternary data.

Example 8-4   A simple procedure for calculating multicomponent vapor-liquid equilibria from binary data is to assume that for the multicomponent mixture

$$g^E = \sum_{\substack{\text{all} \\ \text{binary} \\ \text{pairs}}} g_{ij}^E \tag{8-9.19}$$

solution   To illustrate Eq. (8-9.19), we consider the ternary mixture acetonitrile–benzene–carbon tetrachloride studied by Clarke and Missen [27] at 45°C.

The three sets of binary data were correlated by the Redlich-Kister expansion, which is equivalent to the Margules equation

$$g_{ij}^E = x_i x_j [A + B(x_i - x_j) + C(x_i - x_j)^2 + D(x_i - x_j)^3] \tag{8-9.20}$$

The constants are given in Table 8-12.

When Eq. (8-9.20) for each binary is substituted into Eq. (8-9.19), the excess Gibbs energy of the ternary is obtained. Clarke and Missen compared excess

TABLE 8-12   Redlich-Kister Constants
for the Three Binaries Formed by
Acetonitrile (1), Benzene (2), and
Carbon Tetrachloride (3) at 45°C [see
Eq. (8-9.20)] [27]

Binary system			J/mol		
i	j	A	B	C	D
1	2	2691.6	−33.9	293	0
2	3	317.6	−3.6	0	0
3	1	4745.9	497.5	678.6	416.3

TABLE 8-13   Calculated and
Observed Molar Excess Gibbs
Energies for Acetonitrile (1)–Benzene
(2)–Carbon Tetrachloride (3) at 45°C
[27]

Calculations from Eq. (8-9.19)

Composition		g^E, J/mol	
x_1	x_2	Calc.	Obs.
0.156	0.767	414	431
0.422	0.128	1067	1063
0.553	0.328	808	774
0.673	0.244	711	686
0.169	0.179	690	724
0.289	0.506	711	707

Gibbs energies calculated in this way with those obtained from experimental data for the ternary system according to the definition

$$g^E = RT(x_1 \ln \gamma_1 + x_2 \ln \gamma_2 + x_3 \ln \gamma_3) \qquad (8\text{-}9.21)$$

Calculated and experimental excess Gibbs energies were in good agreement, as illustrated by a few results shown in Table 8-13. Comparison between calculated and experimental results for more than 60 compositions showed that the average deviation (without regard to sign) was only 16 J/mol. Since the uncertainty due to experimental error is about 13 J/mol, Clarke and Missen conclude that Eq. (8-9.19) provides an excellent approximation for this ternary system.

Since accurate experimental studies on ternary systems are not plentiful, it is difficult to say to what extent the positive conclusion of Clarke and Missen can be applied to other systems. It appears that, for mixtures of typical organic fluids, Eq. (8-9.19) usually gives reliable results, although some deviations have been observed, especially for systems with appreciable hydrogen bonding. In many cases the uncertainties introduced by assuming Eq. (8-9.19) are of the same magnitude as the uncertainties due to experimental error in the binary data.

Example 8-5   Although the additivity assumption [Eq. (8-9.19)] often provides a good approximation for strongly nonideal mixtures, there may be noticeable deviations between experimental and calculated multicomponent equilibria. Such deviations, however, are significant only if they exceed experimental uncertainty. To detect significant deviations, data of high accuracy are required, and such data are rare, especially for ternary systems; they are nearly nonexistent for quaternary (and higher) systems. To illustrate, we consider the ternary system chloroform-ethanol-heptane at 50°C studied by Abbott et al. [2]. Highly accurate data were first obtained for the three binary systems. The data were reduced by using Barker's method, as explained by Abbott and Van Ness [3] and elsewhere [97]; the essential feature of this method is that it uses only P-x data (at constant temperature); it does not use data for vapor composition y.

TABLE 8-14   Binary Parameters in Eq. (8-9.22) or (8-9.23) and rms Deviation in Total Pressure for the Systems Chloroform–Ethanol–n-Heptane at 50°C [2]

	Chloroform (1), ethanol (2)	Chloroform (1), heptane (2)	Ethanol (1), heptane (2)
A'_{12}	0.4713	0.3507	3.4301
A'_{21}	1.6043	0.5262	2.4440
α_{12}		0.1505	11.1950
α_{21}		0.1505	2.3806
η		0	9.1369
λ_{12}	−0.3651		
λ_{21}	0.5855		
rms ΔP, bar	0.00075	0.00072	0.00045

solution To represent the binary data, Abbott et al. considered a five-suffix Margules equation and a modified Margules equation

$$\frac{g^E}{RT} = x_1 x_2 [A'_{21} x_1 + A'_{12} x_2 - (\lambda_{21} x_1 + \lambda_{12} x_2) x_1 x_2] \tag{8-9.22}†$$

$$\frac{g^E}{RT} = x_1 x_2 \left(A'_{21} x_1 + A'_{12} x_2 - \frac{\alpha_{12} \alpha_{21} x_1 x_2}{\alpha_{12} x_1 + \alpha_{21} x_2 + \eta x_1 x_2} \right) \tag{8-9.23}†$$

If in Eq. (8-9.22), $\lambda_{21} = \lambda_{12} = D$, and if in Eq. (8-9.23) $\alpha_{12} = \alpha_{21} = D$ and $\eta = 0$, both equations reduce to

$$\frac{g^E}{RT} = x_1 x_2 (A'_{21} x_1 + A'_{12} x_2 - D x_1 x_2) \tag{8-9.24}$$

which is equivalent to the four-suffix Margules equation shown in Table 8-3.
If, in addition, $D = 0$, Eqs. (8-9.22) and (8-9.23) reduce to the three-suffix Margules equation.
For the two binaries chloroform-heptane and chloroform-ethanol, experimental data were reduced by using Eq. (8-9.22); however, for the binary ethanol-heptane, Eq. (8-9.23) was used. Parameters reported by Abbott et al. are shown in Table 8-14. With these parameters, calculated total pressures for each binary are in excellent agreement with those measured.
For the ternary, Abbott and coworkers expressed the excess Gibbs energy by

$$\frac{g^E_{123}}{RT} = \frac{g^E_{12}}{RT} + \frac{g^E_{13}}{RT} + \frac{g^E_{23}}{RT} + (C_0 - C_1 x_1 - C_2 x_2 - C_3 x_3) x_1 x_2 x_3 \tag{8-9.25}$$

where C_0, C_1, C_2, and C_3 are ternary constants and G^E_{ij} is given by Eq. (8-9.22) or (8-9.23) for the ij binary. Equation (8-9.25) successfully reproduced the ternary data within experimental error (rms $\Delta P = 0.0012$ bar).
Abbott et al. considered two simplifications:

Simplification a: $C_0 = C_1 = C_2 = C_3 = 0$

---

†The α's and λ's are not to be confused with those used in the NRTL and Wilson equations.

Simplification b: $C_1 = C_2 = C_3 = 0$ $C_0 = \dfrac{1}{2} \sum_{i \neq j} \sum A'_{ij}$

where the A'_{ij}'s are the binary parameters shown in Table 8-14.

Simplification b was first proposed by Wohl in 1953 [132] on semitheoretical grounds. When calculated total pressures for the ternary system were compared with experimental results, the deviations exceeded the experimental uncertainty.

Simplification	rms ΔP, bar
a	0.0517
b	0.0044

These results suggest that Wohl's approximation (simplification b) provides significant improvement over the additivity assumption for g^E (simplification a). However, one cannot generalize from results for one system. Abbott et al. made similar studies for another ternary (acetone-chloroform-methanol) and found that for this system simplification a gave significantly better results than simplification b, although both simplifications produced errors in total pressure beyond the experimental uncertainty.

Although the results of Abbott and coworkers illustrate the limits of predicting ternary (or higher) vapor-liquid equilibria for nonelectrolyte mixtures from binary data only, these limitations are rarely serious for engineering work unless the system contains an azeotrope. As a practical matter, it is common that experimental uncertainties in binary data are as large as the errors which result when multicomponent equilibria are calculated with some model for g^E by using only parameters obtained from binary data.

Although Eq. (8-9.19) provides a particularly simple approximation, the UNIQUAC equation and the Wilson equation can be generalized to multicomponent mixtures without using that approximation but also without requiring ternary (or higher) parameters. Experience has shown that multicomponent vapor-liquid equilibria can usually be calculated with satisfactory engineering accuracy by using the Wilson equation, the NRTL equation, or the UNIQUAC equation provided that care is exercised in obtaining binary parameters.

Example 8-6   A liquid mixture at 1.013 bar contains 4.7 mole percent ethanol (1), 10.7 mole percent benzene (2), and 84.5 mole percent methylcyclopentane (3). Find the bubble point temperature and the composition of the equilibrium vapor.

solution   There are three unknowns: the bubble point temperature and two vapor phase mole fractions. To find them, we use three equations of equilibrium:

$$y_i \phi_i P = \gamma_i x_i f_i^{0L} \qquad i = 1, 2, 3 \qquad (8\text{-}9.26)$$

where y is the vapor phase mole fraction and x is the liquid phase mole fraction. Fugacity coefficient ϕ_i is given by the truncated virial equation of state

$$\ln \phi_i = \left(2 \sum_{j=1}^{3} y_j B_{ij} - B_M \right) \frac{P}{RT} \tag{8-9.27}$$

where subscript M stands for mixture and

$$B_M = y_1^2 B_{11} + y_2^2 B_{22} + y_3^2 B_{33} + 2y_1 y_2 B_{12} + 2y_1 y_3 B_{13} + 2y_2 y_3 B_{23} \tag{8-9.28}$$

All second virial coefficients B_{ij} are found from the correlation of Hayden and O'Connell as presented in Ref. 48.

The standard-state fugacity f_i^{OL} is the fugacity of pure liquid i at system temperature and system pressure P.

$$f_i^{OL} = P_{vp_i} \phi_i^s \exp\frac{V_i^L (P - P_{vp_i})}{RT} \tag{8-9.29}$$

where P_{vp_i} is the saturation pressure (i.e., the vapor pressure) of pure liquid i, ϕ_i^s is the fugacity coefficient of pure saturated vapor i, and V_i^L is the liquid molar volume of pure i, all at system temperature T.

Activity coefficients are given by the UNIQUAC equation with the following parameters:

Pure Component Parameters

Component	r	q	q'
1	2.11	1.97	0.92
2	3.19	2.40	2.40
3	3.97	3.01	3.01

Binary Parameters

$$\tau_{ij} = \exp\left(-\frac{a_{ij}}{T} \right) \quad \text{and} \quad \tau_{ji} = \exp\left(-\frac{a_{ji}}{T} \right)$$

i	j	a_{ij}, K	a_{ji}, K
1	2	-128.9	997.4
1	3	-118.3	1384
2	3	-6.47	56.47

For a bubble point calculation, a useful objective function $F(1/T)$ is

$$F\left(\frac{1}{T} \right) = \ln\left[\sum_{i=1}^{3} K_i x_i \right] \rightarrow \text{zero}$$

where $K_i = y_i/x_i$. In this calculation, the important unknown is T (rather than y) because P_{vp_i} is a strong function of temperature, whereas ϕ_i is only a weak function of y.

A suitable program for these iterative calculations uses the Newton-Raphson method, as discussed in Ref. [99]. This program requires initial estimates of T and y.

The calculated bubble point temperature is 335.99 K. At this temperature, the second virial coefficients ($cm^3/mole$) and liquid molar volumes ($cm^3/mole$) are:

$$B_{11} = -1155$$

$$B_{12} = B_{21} = -587 \qquad V_1^l = 61.1$$

$$B_{22} = -1086 \qquad V_2^l = 93{,}7$$

$$B_{23} = B_{32} = -1134 \qquad V_3^l = 118$$

$$B_{33} = -1186$$

$$B_{31} = B_{13} = -618$$

$$B_M = -957.3$$

The detailed results at 335.99 K are:

Component	γ_i	f_i^{OL} (bar)	ϕ_i	$100y_i$ Calculated	Observed
1	10.58	0.521	0.980	26.1	25.8
2	1.28	0.564	0.964	7.9	8.4
3	1.03	0.739	0.961	66.0	65.7

The experimental bubble point temperature is 336.15K. Experimental results are from J. E. Sinor and J. H. Weber [113].

In this particular case, there is very good agreement between calculated and experimental results. Such agreement is not unusual, but it is, unfortunately, not guaranteed. For many mixtures of nonelectrolyte liquids (including water), agreement between calculated and observed VLE is somewhat less satisfactory than that shown in this example. However, if there is serious disagreement between calculated and observed VLE, do not give up. There may be some error in the calculation, or there may be some error in the data, or both.

8-10   Estimation of Activity Coefficients

As discussed in Secs. 8-5 and 8-6, activity coefficients in binary liquid mixtures can often be estimated from a few experimental vapor-liquid equilibrium data for the mixtures by using some empirical (or semiempirical) excess function, as shown in Table 8-3. The excess functions provide a thermodynamically consistent method for interpolating and extrapolating limited binary experimental mixture data and for extending binary data to multicomponent mixtures. Frequently, however, few or no mixture data are at hand, and it is necessary to estimate activity coefficients from some suitable correlation. Unfortunately, few such correlations have been established. Theoretical understanding of liquid mixtures is still in an early stage. There has been progress for simple mixtures containing small, spherical, nonpolar molecules, e.g., argon-xenon, but little useful theory is available for mixtures containing larger molecules, especially if they are polar or form hydrogen bonds. Therefore, the few available correlations are essentially empirical. This means that predictions of activity coeffi-

cients can be made only for systems similar to those used to establish the empirical correlation. Even with this restriction, it must be emphasized that, with few exceptions, the accuracy of prediction is not likely to be high whenever predictions for a binary system do not utilize at least some reliable binary data for that system or for another that is closely related. In the following sections we summarize a few of the activity coefficient correlations which are useful for chemical engineering applications.

Regular solution theory

Following ideas first introduced by van der Waals and van Laar, Hildebrand and Scatchard, working independently [54], showed that for binary mixtures of nonpolar molecules, activity coefficients γ_1 and γ_2 can be expressed by

$$RT \ln \gamma_1 = V_1^L \Phi_2^2 (c_{11} + c_{22} - 2c_{12}) \tag{8-10.1}$$

$$RT \ln \gamma_2 = V_2^L \Phi_1^2 (c_{11} + c_{22} - 2c_{12}) \tag{8-10.2}$$

where V_i^L is the liquid molar volume of pure liquid i at temperature T, R is the gas constant, and volume fraction Φ_1 and Φ_2 are defined by

$$\Phi_1 = \frac{x_1 V_1^L}{x_1 V_1^L + x_2 V_2^L} \tag{8-10.3}$$

$$\Phi_2 = \frac{x_2 V_2^L}{x_1 V_1^L + x_2 V_2^L} \tag{8-10.4}$$

with x denoting the mole fraction.

For pure liquid i, the cohesive energy density c_{ii} is defined by

$$c_{ii} = \frac{\Delta U_i}{V_i^L} \tag{8-10.5}$$

where ΔU_i is the energy required isothermally to evaporate liquid i from the saturated liquid to the ideal gas. At temperatures well below the critical,

$$\Delta U_i \approx \Delta H_{v_i} - RT \tag{8-10.6}$$

where ΔH_{v_i} is the molar enthalpy of vaporization of pure liquid i at temperature T.

Cohesive energy density c_{12} reflects intermolecular forces between molecules of component 1 and 2; this is the key quantity in Eqs. (8-10.1) and (8-10.2). Formally, c_{12} can be related to c_{11} and c_{22} by

$$c_{12} = (c_{11}c_{22})^{1/2} (1 - \ell_{12}) \tag{8-10.7}$$

where ℓ_{12} is a binary parameter, positive or negative, but small compared with unity. Upon substitution, Eqs. (8-10.1) and (8-10.2) can be rewritten

$$RT \ln \gamma_1 = V_1^L \Phi_2^2 [(\delta_1 - \delta_2)^2 + 2\ell_{12}\delta_1\delta_2] \qquad (8\text{-}10.8)$$

$$RT \ln \gamma_2 = V_2^L \Phi_1^2 [(\delta_1 - \delta_2)^2 + 2\ell_{12}\delta_1\delta_2] \qquad (8\text{-}10.9)$$

where solubility parameter δ_i is defined by

$$\delta_i = (c_{ii})^{1/2} = \left(\frac{\Delta U_i}{V_i^L}\right)^{1/2} \qquad (8\text{-}10.10)$$

For a first approximation, Hildebrand and Scatchard assume that ℓ_{12} = 0. In that event, Eqs. (8-10.8) and (8-10.9) contain no binary parameter, and activity coefficients γ_1 and γ_2 can be predicted using only pure component data.

Although δ_1 and δ_2 depend on temperature, the theory of regular solutions assumes that the excess entropy is zero. It then follows that, at constant composition,

$$RT \ln \gamma_i = \text{const} \qquad (8\text{-}10.11)$$

Therefore, the right-hand sides of Eqs. (8-10.8) and (8-10.9) may be evaluated at any convenient temperature provided that all quantities are calculated at the same temperature. For many applications the customary convenient temperature is 25°C. A few typical solubility parameters and molar liquid volumes are shown in Table 8-15, and some calculated vapor-liquid equilibria (assuming ℓ_{12} = 0) are shown in Figs. 8-5 to 8-7. For typical nonpolar mixtures, calculated results are often in good agreement with experiment.

The regular solution equations are readily generalized to multicomponent mixtures. For component k

$$RT \ln \gamma_k = V_k^L \sum_i \sum_j (A_{ik} - \tfrac{1}{2}A_{ij})\Phi_i\Phi_j \qquad (8\text{-}10.12)$$

where
$$A_{ij} = (\delta_i - \delta_j)^2 + 2\ell_{ij}\delta_i\delta_j \qquad (8\text{-}10.13)$$

If all binary parameters ℓ_{ij} are assumed equal to zero, Eq. (8-10.12) simplifies to

$$RT \ln \gamma_k = V_k^L(\delta_k - \bar{\delta})^2 \qquad (8\text{-}10.14)$$

where
$$\bar{\delta} = \sum_i \Phi_i\delta_i \qquad (8\text{-}10.15)$$

where the summation refers to all components, including component k.

The simplicity of Eq. (8-10.14) is striking. It says that, in a multicomponent mixture, activity coefficients for all components can be calculated

TABLE 8-15 Molar Liquid Volumes and Solubility Parameters of Some Nonpolar Liquids

	V^L, cm^3 mol^{-1}	δ, (J cm^{-3})$^{1/2}$
Liquefied gases at 90 K:		
Nitrogen	38.1	10.8
Carbon monoxide	37.1	11.7
Argon	29.0	13.9
Oxygen	28.0	14.7
Methane	35.3	15.1
Carbon tetrafluoride	46.0	17.0
Ethane	45.7	19.4
Liquid solvents at 25°C:		
Perfluoro-n-heptane	226	12.3
Neopentane	122	12.7
Isopentane	117	13.9
n-Pentane	116	14.5
n-Hexane	132	14.9
1-Hexene	126	14.9
n-Octane	164	15.3
n-Hexadecane	294	16.3
Cyclohexane	109	16.8
Carbon tetrachloride	97	17.6
Ethyl benzene	123	18.0
Toluene	107	18.2
Benzene	89	18.8
Styrene	116	19.0
Tetrachloroethylene	103	19.0
Carbon disulfide	61	20.5
Bromine	51	23.5

at any composition and temperature by using only solubility parameters and molar liquid volumes for the pure components. For mixtures of hydrocarbons, Eq. (8-10.14) often provides a good approximation.

Although binary parameter ℓ_{12} is generally small compared with unity in nonpolar mixtures, its importance may be significant, especially if the
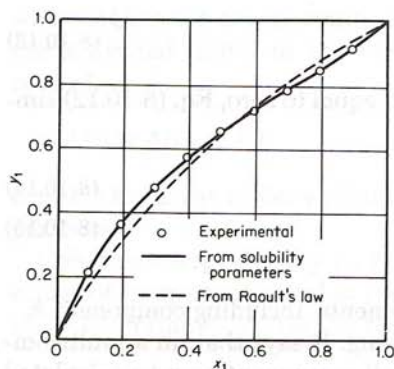
Figure 8-5 Vapor-liquid equilibria for benzene (1)–normal heptane (2) at 70°C. *(From Ref. 97.)*
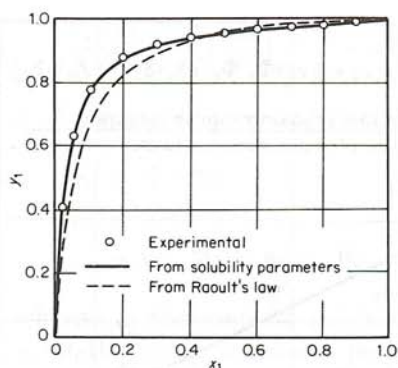
Figure 8-6 Vapor-liquid equilibria for carbon monoxide (1)–methane (2) at 90.7 K. *(From Ref. 97.)*

difference between δ_1 and δ_2 is small. To illustrate, suppose $T = 300$ K, $V_1^L = 100 \text{ cm}^3/\text{mol}$, $\delta_1 = 14.3$, and $\delta_2 = 15.3 \ (\text{J/cm}^3)^{1/2}$. At infinite dilution ($\Phi_2 = 1$) we find from Eq. (8-10.8) that $\gamma_1^\infty = 1.04$ when $\ell_{12} = 0$. However, if $\ell_{12} = 0.01$, we obtain $\gamma_1^\infty = 1.24$, and if $\ell_{12} = 0.03$, $\gamma_1^\infty = 1.77$. These illustrative results indicate that calculated activity coefficients are often sensitive to small values of ℓ_{12} and that much improvement in predicted results can often be achieved when just one binary datum is available for evaluating ℓ_{12}.

Efforts to correlate ℓ_{12} have met with little success. In their study of binary cryogenic mixtures, Bazúa and Prausnitz [13] found no satisfactory variation of ℓ_{12} with pure component properties, although some rough trends were found by Cheung and Zander [26] and by Preston and Prausnitz [101]. In many typical cases ℓ_{12} is positive and becomes larger as the differences in molecular size and chemical nature of the components increase. For example, for carbon dioxide–paraffin mixtures at low temperatures, Preston found that $\ell_{12} = -0.02$ (methane); $+0.08$ (ethane); $+0.08$ (propane); $+0.09$ (butane).
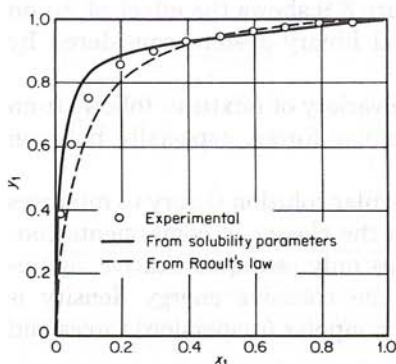
Figure 8-7 Vapor–liquid equilibria for neopentane (1)–carbon tetrachloride (2) at 0°C. *(From Ref. 97.)*
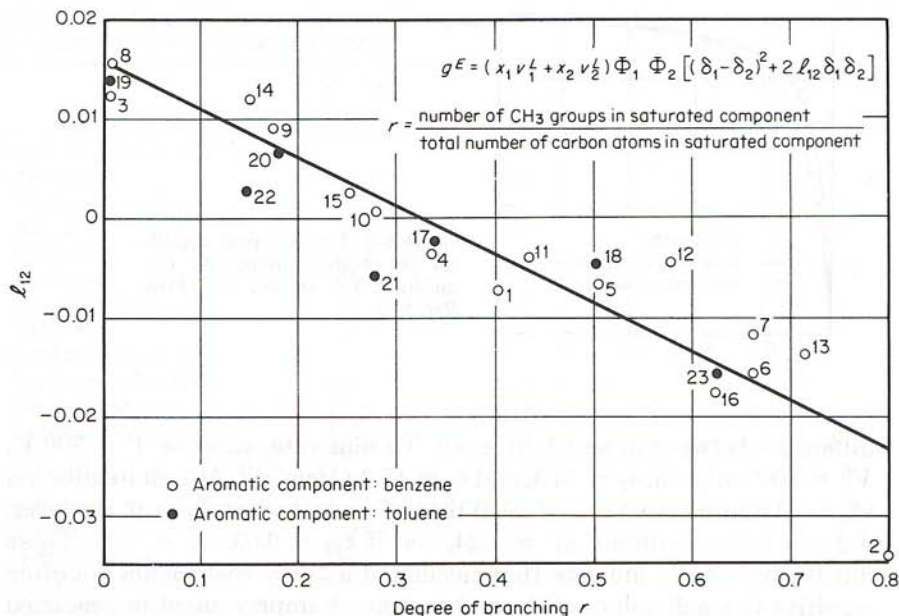
Figure 8-8 Correlation of the excess Gibbs energy for aromatic–saturated hydrocarbon mixtures at 50°C. Numbers relate to list of binary systems in Ref. 38, table 1. *(From Ref. 38.)*

Since ℓ_{12} is an essentially empirical parameter, it depends on temperature. However, for typical nonpolar mixtures over a modest range of temperature, that dependence is usually small.

For mixtures of aromatic and saturated hydrocarbons, Funk and Prausnitz [38] found a systematic variation of ℓ_{12} with the structure of the saturated component, as shown in Fig. 8-8. In that case a good correlation could be established because experimental data are relatively plentiful and because the correlation is severely restricted with respect to the chemical nature of the components. Figure 8-9 shows the effect of ℓ_{12} on calculating relative volatility in a typical binary system considered by Funk and Prausnitz.

Our inability to correlate ℓ_{12} for a wide variety of mixtures follows from our lack of understanding of intermolecular forces, especially between molecules at short separations.

Several authors have tried to extend regular solution theory to mixtures containing polar components; but unless the classes of components considered are restricted, such extension has only semiquantitative significance. In establishing the extensions, the cohesive energy density is divided into separate contributions from nonpolar (dispersion) forces and from polar forces:

$$\left(\frac{\Delta U}{V^L}\right)_{total} = \left(\frac{\Delta U}{V^L}\right)_{nonpolar} + \left(\frac{\Delta U}{V^L}\right)_{polar} \tag{8-10.16}$$

Equations (8-10.1) and (8-10.2) are used with the substitutions

$$c_{11} = \tau_1^2 + \lambda_1^2 \tag{8-10.17}$$

$$c_{22} = \tau_2^2 + \lambda_2^2 \tag{8-10.18}$$

$$c_{12} = \lambda_1\lambda_2 + \tau_1\tau_2 + \psi_{12} \tag{8-10.19}$$

where λ_i is the nonpolar solubility parameter $[\lambda_i^2 = (\Delta U_i/V_i^L)_{nonpolar}]$ and τ_i is the polar solubility parameter $[\tau_i^2 = (\Delta U_i/V_i^L)_{polar}]$. The binary parameter ψ_{12} is not negligible, as shown by Weimer and Prausnitz [128] in their correlation of activity coefficients at infinite dilution for hydrocarbons in polar non-hydrogen-bonding solvents.

Further extension of the Scatchard-Hildebrand equation to include hydrogen-bonded components makes little sense theoretically, since the
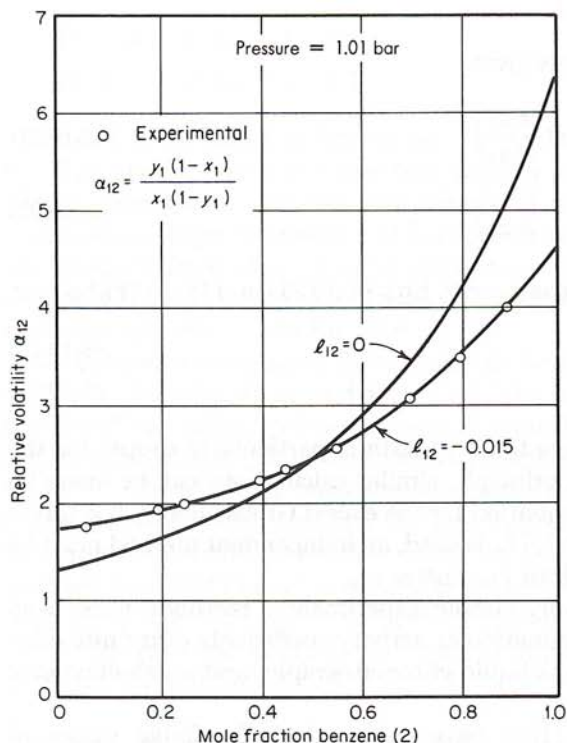
Figure 8-9 Comparison of experimental volatilities with volatilities calculated by Scatchard-Hildebrand theory for 2,2-dimethylbutane (1)–benzene (2). *(From Ref. 38.)*

assumptions of regular solution theory are seriously in error for mixtures containing such components. Nevertheless, some semiquantitative success has been achieved by Hansen et al. [47] and others [25] interested in establishing criteria for formulating solvents for paints and other surface coatings. Also, Null and Palmer [85] have used extended solubility parameters for establishing an empirical correlation of activity coefficients.

Activity coefficients at infinite dilution

Experimental activity coefficients at infinite dilution are particularly useful for calculating the parameters needed in an expression for the excess Gibbs energy (Table 8-3). In a binary mixture, suppose experimental data are available for infinite-dilution activity coefficients γ_1^∞ and γ_2^∞. These can be used to evaluate two adjustable constants in any desired expression for g^E. For example, consider the van Laar equation

$$g^E = A x_1 x_2 \left(x_1 \frac{A}{B} + x_2 \right)^{-1} \tag{8-10.20}$$

As indicated in Sec. 8-5, this gives

$$RT \ln \gamma_1 = A \left(1 + \frac{A}{B} \frac{x_1}{x_2} \right)^{-2} \tag{8-10.21}$$

and

$$RT \ln \gamma_2 = B \left(1 + \frac{B}{A} \frac{x_2}{x_1} \right)^{-2} \tag{8-10.22}$$

In the limit, as $x_1 \to 0$ or as $x_2 \to 0$, Eqs. (8-10.21) and (8-10.22) become

$$RT \ln \gamma_1^\infty = A \tag{8-10.23}$$

and

$$RT \ln \gamma_2^\infty = B \tag{8-10.24}$$

Calculation of parameters from γ^∞ data is particularly simple for the van Laar equation, but in principle, similar calculations can be made by using any two-parameter equation for the excess Gibbs energy. If a three-parameter equation, e.g., NRTL, is used, an independent method must be chosen to determine the third parameter α_{12}.

In recent years, relatively simple experimental methods have been developed for rapid determination of activity coefficients at infinite dilution. These are based on gas-liquid chromatography and on ebulliometry [13, 62, 85, 135, 137, 138].

Schreiber and Eckert [109] have shown that if reliable values of γ_1^∞ and γ_2^∞ are available, either from direct experiment or from a correla-

TABLE 8-16   Fit of Binary Data Using Limiting Activity Coefficients in the Wilson Equation [109]

System and γ^∞	Temp., °C	Average absolute error in calc. $y \times 10^3$	
		All points	γ_1^∞ and γ_2^∞ only
Acetone (1.65)–benzene (1.52)	45	2	4
Carbon tetrachloride (5.66)–acetonitrile (9.30)	45	7	11
Ethanol (18.1)–n-hexane (9.05)	69–79	10	12
Chloroform (2.00)–methanol (9.40)	50	10	28
Acetone (8.75)–water (3.60)	100	10	15

tion, it is possible to predict vapor-liquid equilibria over the entire range of composition. For completely miscible mixtures the Wilson equation is particularly useful. Parameters Λ_{12} and Λ_{21} are found from simultaneous solution of the relations

$$\ln \gamma_1^\infty = -\ln \Lambda_{12} - \Lambda_{21} + 1 \tag{8-10.25}$$

$$\ln \gamma_2^\infty = -\ln \Lambda_{21} - \Lambda_{12} + 1 \tag{8-10.26}$$

Table 8-16 shows some typical results obtained by Schreiber and Eckert. The average error in vapor composition using γ^∞ data alone is only slightly larger than that obtained when γ data are used over the entire composition range. Schreiber and Eckert also show that reasonable results are often obtained when γ_1^∞ or γ_2^∞ (but not both) are used. When only one γ^∞ is available, it is necessary to use the one-parameter Wilson equation, as discussed earlier. [See Eq. (8-5.12).]

An extensive correlation for γ^∞ data in binary systems has been presented by Pierotti, Deal, and Derr [91]. This correlation can be used to predict γ^∞ for water, hydrocarbons, and typical organic components, e.g., esters, aldehydes, alcohols, ketones, nitriles, in the temperature region 25 to 100°C. The pertinent equations and tables are summarized by Treybal [123] and, with slight changes, are reproduced in Tables 8-17 and 8-18. The accuracy of the correlation varies considerably from one system to another; provided that γ^∞ is not one or more orders of magnitude removed from unity, the average deviation in γ^∞ is about 8 percent.

To illustrate use of Table 8-17, an example, closely resembling one given by Treybal, follows.

Example 8-7   Estimate infinite-dilution activity coefficients for the ethanol-water binary system at 100°C. (Solution appears on p. 299.)

TABLE 8-17 Correlating Constants for Activity Coefficients at Infinite Dilution; Homologous Series of Solutes and Solvents [91]

Solute (1)	Solvent (2)	Temp., °C	α	ε	ζ	η	θ	Eq.
n-Acids	Water	25	−1.00	0.622	0.490	...	0	(a)
		50	−0.80	0.590	0.290	...	0	(a)
		100	−0.620	0.517	0.140	...	0	(a)
n-Primary alcohols	Water	25	−0.995	0.622	0.558	...	0	(a)
		60	−0.755	0.583	0.460	...	0	(a)
		100	−0.420	0.517	0.230	...	0	(a)
n-Secondary alcohols	Water	25	−1.220	0.622	0.170	0	...	(b)
		60	−1.023	0.583	0.252	0	...	(b)
		100	−0.870	0.517	0.400	0	...	(b)
n-Tertiary alcohols	Water	25	−1.740	0.622	0.170	...	...	(c)
		60	−1.477	0.583	0.252	...	...	(c)
		100	−1.291	0.517	0.400	...	...	(c)
Alcohols, general	Water	25	−0.525	0.622	0.475	0	...	(d)
		60	−0.33	0.583	0.39	0	...	(d)
		100	−0.15	0.517	0.34	0	...	(d)
n-Allyl alcohols	Water	25	−1.180	0.622	0.558	...	0	(a)
		60	−0.929	0.583	0.460	...	0	(a)
		100	−0.650	0.517	0.230	...	0	(a)
n-Aldehydes	Water	25	−0.780	0.622	0.320	...	0	(a)
		60	−0.400	0.583	0.210	...	0	(a)
		100	−0.03	0.517	0	...	0	(a)
n-Alkene aldehydes	Water	25	−0.720	0.622	0.320	...	0	(a)
		60	−0.540	0.583	0.210	...	0	(a)
		100	−0.298	0.517	0	...	0	(a)

	Solvent	Temp.						Ref.
n-Ketones	Water	25	−1.475	0.622	0.500	0	⋮	(b)
		60	−1.040	0.583	0.330	0	⋮	(b)
		100	−0.621	0.517	0.200	0	⋮	(b)
n-Acetals	Water	25	−2.556	0.622	0.486	⋮	⋮	(e)
		60	−2.184	0.583	0.451	⋮	⋮	(e)
		100	−1.780	0.517	0.426	⋮	⋮	(e)
n-Ethers	Water	20	−0.770	0.640	0.195	0	⋮	(b)
n-Nitriles	Water	25	−0.587	0.622	0.760	⋮	0	(a)
		60	−0.368	0.583	0.413	⋮	0	(a)
		100	−0.095	0.517	0	⋮	0	(a)
n-Alkene nitriles	Water	25	−0.520	0.622	0.760	⋮	0	(a)
		60	−0.323	0.583	0.413	⋮	0	(a)
		100	−0.074	0.517	0	⋮	0	(a)
n-Esters	Water	20	−0.930	0.640	0.260	0	⋮	(b)
n-Formates	Water	20	−0.585	0.640	0.260	⋮	0	(a)
n-Monoalkyl chlorides	Water	20	1.265	0.640	0.073	⋮	0	(a)
n-Paraffins	Water	16	0.688	0.642	0	⋮	0	(a)
n-Alkyl benzenes	Water	25	3.554	0.622	−0.466	⋮	⋮	(f)
n-Alcohols	Paraffins	25	1.960	0	0.475	−0.00049	⋮	(d)
		60	1.460	0	0.390	−0.00057	⋮	(d)
		100	1.070	0	0.340	−0.00061	⋮	(d)
n-Ketones	Paraffins	25	0.0877	0	0.757	−0.00049	⋮	(b)
		60	0.016	0	0.680	−0.00057	⋮	(b)
		100	−0.067	0	0.605	−0.00061	⋮	(b)

TABLE 8-17 Correlating Constants for Activity Coefficients at Infinite Dilution; Homologous Series of Solutes and Solvents (Continued)

Solute (1)	Solvent (2)	Temp., °C	α	ϵ	ζ	η	θ	Eq.
Water	n-Alcohols	25	0.760	0	0	...	−0.630	(a)
		60	0.680	0	0	...	−0.440	(a)
		100	0.617	0	0	...	−0.280	(a)
Water	sec-Alcohols	80	1.208	0	0	...	−0.690	(c)
Water	n-Ketones	25	1.857	0	0	...	−1.019	(c)
		60	1.493	0	0	...	−0.73	(c)
		100	1.231	0	0	...	−0.557	(c)
Ketones	n-Alcohols	25	−0.088	0.176	0.50	−0.00049	−0.630	(g)
		60	−0.035	0.138	0.33	−0.00057	−0.440	(g)
		100	−0.035	0.112	0.20	−0.00061	−0.280	(g)
Aldehydes	n-Alcohols	25	−0.701	0.176	0.320	−0.00049	−0.630	(h)
		60	−0.239	0.138	0.210	−0.00057	−0.440	(h)
Esters	n-Alcohols	25	0.212	0.176	0.260	−0.00049	−0.630	(g)
		60	0.055	0.138	0.240	−0.00057	−0.440	(g)
		100	0	0.112	0.220	−0.00061	−0.280	(g)
Acetals	n-Alcohols	60	−1.10	0.138	0.451	−0.00057	−0.440	(i)
Paraffins	Ketones	25	...	0.1821	...	−0.00049	0.402	(j)
		60	...	0.1145	...	−0.00057	0.402	(j)
		90	...	0.0746	...	−0.00061	0.402	(j)

Equations

(a) $\log \gamma_i^\infty = \alpha + \epsilon N_1 + \frac{\zeta}{N_1} + \frac{\theta}{N_2}$

(b) $\log \gamma_i^\infty = \alpha + \epsilon N_1 + \zeta\left(\frac{1}{N_1'} + \frac{1}{N_1''}\right) + \eta(N_1 - N_2)^2 + \theta\left(\frac{1}{N_2'} + \frac{1}{N_2''}\right)$

(c) $\log \gamma_i^\infty = \alpha + \epsilon N_1 + \zeta\left(\frac{1}{N_1'} + \frac{1}{N_1''} + \frac{1}{N_1'''}\right) + \eta(N_1 - N_2)^2$

(d) $\log \gamma_i^\infty = \alpha + \epsilon N_1 + \zeta\left(\frac{1}{N_1'} + \frac{1}{N_1''} + \frac{1}{N_1'''} - 3\right) + \eta(N_1 - N_2)^2$

(e) $\log \gamma_i^\infty = \alpha + \epsilon N_1 + \zeta\left(\frac{1}{N_1'} + \frac{1}{N_1''} + \frac{2}{N_1'''}\right)$

(f) $\log \gamma_i^\infty = \alpha + \epsilon N_1 + \zeta\left(\frac{1}{N_1} - 4\right)$

(g) $\log \gamma_i^\infty = \alpha + \epsilon \frac{N_1}{N_2} + \zeta\left(\frac{1}{N_1'} + \frac{1}{N_1''}\right) + \eta(N_1 - N_2)^2 + \frac{\theta}{N_2}$

(h) $\log \gamma_i^\infty = \alpha + \epsilon \frac{N_1}{N_2} + \frac{\zeta}{N_1} + \eta(N_1 - N_2)^2 + \frac{\theta}{N_2}$

(i) $\log \gamma_i^\infty = \alpha + \epsilon \frac{N_1}{N_2} + \zeta\left(\frac{1}{N_1'} + \frac{1}{N_1''} + \frac{2}{N_1'''}\right) + \eta(N_1 - N_2)^2 + \frac{\theta}{N_2}$

(j) $\log \gamma_i^\infty = \epsilon \frac{N_1}{N_2} + \eta(N_1 - N_2)^2 + \theta\left(\frac{1}{N_2'} + \frac{1}{N_2''}\right)$

N_1, N_2 = total number of carbon atoms in molecules 1 and 2, respectively

N', N'', N''' = number of carbon atoms in respective branches of branched compounds, counting the polar grouping; thus, for t-butanol,
$N' = N'' = N''' = 2$

TABLE 8-18 Correlating Constants for Activity Coefficients at Infinite Dilution; Homologous Series of Hydrocarbons in Specific Solvents [91]

Temperature, °C	η		Heptane	Methyl ethyl ketone	Furfural	Phenol	Ethanol	Triethylene glycol	Diethylene glycol	Ethylene glycol
							Solvent			
							Value of ϵ			
25	−0.00049		0	0.0455	0.0937	0.0625	0.088	...	0.191	0.275
50	−0.00055		0	0.033	0.0878	0.0590	0.073	0.161	0.179	0.249
70	−0.00058		0	0.025	0.0810	0.0586	0.065	...	0.173	0.236
90	−0.00061		0	0.019	0.0686	0.0581	0.059	0.134	0.158	0.226
							Value of θ			
25			0.2105	0.1435	0.1152	0.1421	0.2125	0.181	0.2022	0.275
70			0.1668	0.1142	0.0836	0.1054	0.1575	0.129	0.1472	0.2195
130			0.1212	0.0875	0.0531	0.0734	0.1035	0.0767	0.0996	0.1492
							Value of κ			
25			0.1874	0.2079	0.2178	0.2406	0.2425	0.3124	0.3180	0.4147
70			0.1478	0.1754	0.1675	0.1810	0.1753	0.2406	0.2545	0.3516
130			0.1051	0.1427	0.1185	0.1480	0.1169	0.1569	0.1919	0.2772
							Value of α			
25			0	0.335	0.916	0.870	0.580	...	0.875	1.208
50			0	0.332	0.756	0.755	0.570	0.72	0.815	1.154
70			0	0.331	0.737	0.690	0.590	...	0.725	1.089
90			0	0.330	0.771	0.620	0.610	0.68	0.72	

Solute (1)	Eq.	ζ
Paraffins	(a)	0
		0
		0
		0

Alkyl cyclohexanes										
25	(a)	−0.260	0.18	0.70	1.26	1.20	1.06	...	1.675	2.36
50		−0.220	...	0.650	1.120	1.040	1.01	1.46	1.61	2.22
70		−0.195	0.131	0.581	1.020	0.935	0.972	...	1.550	2.08
90		−0.180	0.09	0.480	0.930	0.843	0.925	1.25	1.505	
Alkyl benzenes										
25	(a)	−0.466	0.328	0.277	0.67	0.694	1.011	...	1.08	
50		−0.390	0.243	...	0.55	0.580	0.938	0.80	1.00	1.595
70		−0.362	0.225	0.240	0.45	0.500	0.900	...	0.96	1.51
90		−0.350	0.202	0.239	0.44	0.420	0.862	0.74	0.935	1.43
Alkyl naphthalenes										
25	(a)	−0.10	0.53	0.169	0.46	0.595	1.06	...	1.00	
50		−0.14	0.53	0.141	0.40	0.54	1.03	0.75	1.00	1.92
70		−0.173	0.53	0.215	0.39	0.497	1.02	...	0.991	1.82
90		−0.204	0.53	0.232	...	0.445	...	0.83	1.01	1.765
Alkyl tetralins										
25	(a)	0.28	0.244	0.179	0.652	0.378	...	...	1.43	
50		0.24	...	...	0.528	0.364	...	1.00	1.38	
70		0.21	0.220	0.217	0.447	0.371	...	...	1.33	
90		0.19	...	...	0.373	0.348	...	0.893	1.28	
Alkyl decalins										
25	(a)	−0.43	...	0.871	1.54	1.411	...	...	2.46	
50		−0.368	...	...	1.367	1.285	...	1.906	2.25	
70		−0.355	0.356	0.80	1.253	1.161	...	...	2.07	
90		−0.320	...	...	1.166	1.078	...	1.68	2.06	
Unalkylated aromatics, naphthenes, naphthene aromatics										
25	(b)	1.176† 1.845‡	−1.072	−0.7305	−0.230	−0.383	−0.485	−0.406	−0.377	−0.154
70		0.846† 1.362‡	−0.886	−0.625	−0.080	−0.226	−0.212	−0.186	−0.0775	−0.0174
130		0.544† 0.846‡	−0.6305	−0.504	+0.020	−0.197	+0.47	+0.095	+0.181	+0.229

TABLE 8-18 Correlating Constants for Activity Coefficients at Infinite Dilution; Homologous Series of Hydrocarbons in Specific Solvents (*Continued*)

Equations

(a) $\log \gamma_1^\infty = \alpha + \epsilon N_p + \dfrac{\zeta}{N_p + 2} + \eta (N_1 + N_2)^2$

(b) $\log \gamma_1^\infty = \alpha + \theta N_a + \kappa N_n + \xi \left(\dfrac{1}{r} - 1 \right)$

where N_1, N_2 = total number of carbon atoms in molecules 1 and 2, respectively

N_p = number of paraffinic carbon atoms in solute

N_a = number of aromatic carbon atoms, including $=C-$, $=CH-$, ring-juncture naphthenic carbons $-\overset{|}{\underset{|}{C}}-$, and naphthenic carbons in the α position to an aromatic nucleus

N_n = number of naphthenic carbon atoms not counted in N_a

r = number of rings

Examples:

Butyl decalin:	$N_p = 4$	$N_a = 2$	$N_n = 8$	$N_1 = 14$	$r = 2$
Butyl tetralin:	$N_p = 4$	$N_a = 8$	$N_n = 2$	$N_1 = 14$	$r = 2$

solution First we find γ^∞ for ethanol. Subscript 1 stands for ethanol, and subscript 2 stands for water. From Table 8-17, $\alpha = -0.420$, $\epsilon = 0.517$, $\zeta = 0.230$, $\theta = 0$, and $N_1 = 2$. Using Eq. (a) at the end of Table 8-17, we have

$$\log \gamma^\infty = -0.420 + (0.517)(2) + \frac{0.230}{2} = 0.729$$

$$\gamma^\infty \text{ (ethanol)} = 5.875$$

Next, for water, we again use Table 8-17. Now subscript 1 stands for water and subscript 2 stands for ethanol.

$$\alpha = 0.617 \qquad \epsilon = \zeta = 0 \qquad \theta = -0.280 \qquad N_2 = 2$$

$$\log \gamma^\infty = 0.617 - \frac{0.280}{2} = 0.477$$

$$\gamma^\infty \text{ (water)} = 3.0$$

These calculated results are in good agreement with experimental data of Jones et al. [59].

An alternative method for estimating activity coefficients at infinite dilution is provided by a modified regular solution theory. MOSCED (modified separation of cohesive energy density) is a model proposed by Thomas and Eckert [119] for predicting limiting activity coefficients (γ^∞'s) from pure component parameters only. It is essentially an extension of regular solution theory to polar and associating systems. The extension is based on the assumption that forces contributing to the cohesive energy density are additive. Forces included are dispersion, orientation, induction, and hydrogen bonding. The five parameters associated with these forces are the dispersion parameter λ, the induction parameter q, the polar parameter τ, and the acidity α and basicity β parameters. These modifications affect the magnitudes of the activity coefficients, but they do so in a symmetric way; both γ_1^∞ and γ_2^∞ are affected the same way, contrary to experiment. To account for asymmetry, Thomas and Eckert introduce two more parameters, ψ and ξ, to account for asymmetry effects resulting from differences in polarity and degree of hydrogen bonding, respectively. These two are functions of the other parameters.

A summary of the equation and a list of the parameters for 144 substances at 20°C are given in Table 8-19. In a binary mixture, the activity coefficient for component 2 at infinite dilution is

$$\ln \gamma_2^\infty = \frac{v_2}{RT} \left[(\lambda_1 - \lambda_2)^2 + \frac{q_1^2 q_2^2 (\tau_1 - \tau_2)^2}{\psi_1} \right.$$
$$\left. + \frac{(\alpha_1 - \alpha_2)(\beta_1 - \beta_2)}{\xi_1} \right] + d_{12} \qquad (8\text{-}10.27)$$

There is a corresponding expression for $\ln \gamma_1^\infty$. Here, v_2 is liquid molar volume at 20°C in $cm^3 \, mol^{-1}$ and d_{12} is a Flory-Huggins combinatorial term to account for differences in molecular size:

$$d_{12} = \ln \left(\frac{v_2}{v_1} \right)^{aa} + 1 - \left(\frac{v_2}{v_1} \right)^{aa} \qquad (8\text{-}10.28)$$

TABLE 8-19   Parameters for MOSCED Model at 20°C

RI	v	λ	τ	q	α	β	ψ	ξ	aa	ID	Compound
1.628	72.0	9.80	0.30	1.00	0.29	0.16	1.00	1.00	0.952	1	Carbon disulfide
1.460	96.5	8.58	0.87	1.00	0.58	0.15	1.02	1.01	0.945	1	Carbon tetrachloride
1.506	98.5	9.05	1.00	1.00	0.70	0.10	1.02	1.02	0.943	1	Bromotrichloromethane
1.446	80.7	8.43	1.95	1.00	3.05	0.06	1.16	1.11	0.914	1	Chloroform
1.496	82.7	8.95	2.00	1.00	2.90	0.10	1.17	1.12	0.911	1	Bromodichloromethane
1.424	64.1	8.20	2.79	1.00	2.49	0.38	1.42	1.33	0.868	1	Dichloromethane
1.542	69.6	9.41	2.90	1.00	2.00	0.10	1.45	1.31	0.870	1	Dibromomethane
1.328	40.5	7.14	2.55	1.00	7.45	7.45	1.94	3.62	0.353	1	Methanol
1.381	53.7	7.73	6.24	1.00	1.30	2.40	2.18	2.06	0.546	1	Nitromethane
1.531	79.1	9.30	1.95	1.00	0.35	0.29	1.16	1.11	0.915	1	Methyl iodide
1.344	52.2	7.43	5.99	1.00	0.86	3.98	2.17	2.10	0.573	1	Acetonitrile
1.438	99.6	8.35	1.40	1.00	0.50	0.20	1.06	1.04	0.933	1	1,1,1-Trichloroethane
1.471	92.7	8.70	2.40	1.00	1.50	0.20	1.28	1.20	0.984	1	1,1,2-Trichloroethane
1.445	79.1	8.42	3.13	1.00	0.79	0.51	1.53	1.37	0.854	1	1,2-Dichloroethane
1.416	84.2	8.12	2.20	1.00	1.00	0.30	1.22	1.16	0.903	1	1,1-Dichloroethane
1.392	72.0	7.85	4.85	1.00	0.29	2.20	2.04	1.73	0.719	1	Nitroethane
1.513	93.6	9.12	1.66	1.00	0.31	0.27	1.10	1.07	0.926	1	Ethyl iodide
1.424	76.5	8.20	2.04	1.00	0.32	0.23	1.18	1.12	0.912	1	Ethyl bromide
1.361	58.4	7.51	1.36	1.00	6.19	6.19	1.48	3.43	0.564	1	Ethanol
1.366	70.4	7.57	4.82	1.00	0.38	3.31	2.04	1.78	0.716	1	Propionitrile
1.359	74.4	7.49	4.10	1.00	0.00	4.87	1.86	1.58	0.790	1	Acetone
1.360	80.4	7.50	3.32	1.00	0.00	3.83	1.60	1.41	0.846	1	Ethyl formate
1.361	79.3	7.52	3.32	1.00	0.00	3.83	1.60	1.41	0.846	1	Methyl acetate
1.402	89.0	7.96	4.15	1.00	0.25	1.88	1.88	1.61	0.782	1	1-Nitropropane
1.430	77.0	8.26	4.62	1.00	0.65	10.30	2.06	2.46	0.682	1	Dimethylformamide
1.394	90.1	7.88	4.13	1.00	0.23	1.85	1.87	1.61	0.784	1	2-Nitropropane
1.503	111.6	8.83	1.40	1.00	0.14	0.15	1.06	1.04	0.934	1	2-Propyl iodide
1.388	88.1	7.81	1.90	1.00	0.30	0.18	1.15	1.10	0.918	1	n-Propyl chloride
1.434	90.9	8.31	1.74	1.00	0.27	0.20	1.12	1.08	0.923	1	n-Propyl bromide
1.290	88.1	6.70	0.00	1.00	0.00	0.00	1.00	1.00	0.953	1	Propane
1.386	74.8	7.79	1.16	1.00	5.28	5.28	1.34	3.34	0.670	1	Propanol
1.379	89.6	7.71	3.25	1.00	0.00	4.05	1.57	1.39	0.851	1	Butanone
1.378	96.3	7.69	2.84	1.00	0.00	3.28	1.42	1.29	0.875	1	Methyl propionate
1.407	81.1	8.02	2.30	1.00	0.00	4.58	1.25	1.17	0.902	1	Tetrahydrofuran
1.377	97.3	7.69	2.84	1.00	0.00	3.28	1.42	1.29	0.875	1	Propyl formate
1.372	97.8	7.64	2.84	1.00	0.00	3.28	1.42	1.29	0.875	1	Ethyl acetate
1.422	84.2	8.08	3.32	1.00	0.00	4.14	1.60	1.41	0.846	1	Dioxane
1.397	106.0	7.91	1.62	1.00	0.25	0.15	1.09	1.06	0.927	1	2-Chlorobutane
1.402	104.5	7.96	1.66	1.00	0.26	0.16	1.10	1.07	0.926	1	n-Butyl chloride
1.386	109.9	7.79	1.60	1.00	0.25	0.15	1.09	1.06	0.928	1	tert-Butyl chloride
1.440	107.4	8.37	1.52	1.00	0.24	0.17	1.08	1.05	0.930	1	n-Butyl bromide
1.333	100.4	7.20	0.00	1.00	0.00	0.00	1.00	1.00	0.953	1	Butane
1.399	91.5	7.93	1.02	1.00	4.62	4.62	1.26	3.17	0.736	1	Butanol
1.510	80.5	8.57	3.16	0.90	0.68	6.70	1.40	1.72	0.812	3	Pyridine
1.430	100.8	8.27	0.58	0.80	0.00	0.37	1.00	1.00	0.950	1	trans-1,3-Pentadiene
1.422	100.0	8.18	0.52	0.80	0.00	0.34	1.00	1.00	0.950	1	Isoprene
1.407	94.1	8.01	0.00	1.00	0.00	0.00	1.00	1.00	0.953	1	Cyclopentane
1.387	105.9	7.80	0.26	0.90	0.00	0.21	1.00	1.00	0.952	1	Isopentene
1.383	107.0	7.76	0.25	0.90	0.00	0.21	1.00	1.00	0.952	1	2-Pentene
1.371	109.6	7.62	0.25	1.00	0.00	0.20	1.00	1.00	0.952	1	1-Pentene
1.338	107.8	7.25	0.26	1.00	0.00	0.21	1.00	1.00	0.952	1	3-Methyl-1-butene
1.364	111.8	7.55	0.25	0.90	0.00	0.21	1.00	1.00	0.952	1	2-Methyl-1-butene
1.388	107.3	7.81	2.50	1.00	0.00	3.20	1.31	1.21	0.893	2	Methyl isopropyl ketone
1.453	90.9	8.51	1.10	1.00	4.50	4.50	1.25	3.13	0.745	1	Cyclopentanol
1.392	105.8	7.86	2.77	1.00	0.00	3.43	1.40	1.27	0.879	1	3-Pentanone
1.390	106.5	7.83	2.77	1.00	0.00	3.43	1.40	1.27	0.879	1	2-Pentanone
1.384	115.0	7.77	2.48	1.00	0.00	2.86	1.30	1.21	0.893	1	Propyl acetate
1.388	113.7	7.81	2.48	1.00	0.00	2.86	1.30	1.21	0.893	1	Methyl butylate
1.384	114.5	7.77	2.48	1.00	0.00	2.86	1.30	1.21	0.893	1	Ethyl propionate
1.445	124.0	8.42	1.36	1.00	0.21	0.15	1.06	1.04	0.935	1	n-Pentyl bromide
1.358	115.3	7.48	0.00	1.00	0.00	0.00	1.00	1.00	0.953	1	Pentane
1.354	116.4	7.43	0.00	1.00	0.00	0.00	1.00	1.00	0.953	1	Isopentane
1.410	108.1	8.05	0.90	1.00	4.12	4.12	1.20	2.93	0.781	1	1-Pentanol
1.552	102.3	8.95	3.78	0.90	0.63	1.36	1.51	1.38	0.806	3	Nitrobenzene
1.525	101.8	8.71	1.84	0.90	0.75	0.45	1.09	1.07	0.917	3	Chlorobenzene
1.501	89.1	8.49	1.95	0.90	0.22	0.56	1.11	1.07	0.915	3	Benzene
1.551	89.0	8.94	2.16	0.90	16.20	1.64	1.43	3.39	0.651	3	Phenol

RI	v	λ	τ	q	α	β	ψ	ξ	aa	ID	Compound
1.586	91.1	9.25	4.22	0.90	3.81	2.13	1.68	2.39	0.702	3	Aniline
1.447	101.4	8.44	0.28	0.92	0.00	0.25	1.00	1.00	0.952	2	Cyclohexene
1.451	103.6	8.48	3.05	1.00	0.00	4.82	1.50	1.34	0.863	2	Cyclohexanone
1.392	123.8	7.85	0.23	0.92	0.00	0.18	1.00	1.00	0.952	1	4-Methyl-1-pentene
1.426	108.1	8.22	0.00	1.00	0.00	0.00	1.00	1.00	0.953	2	Cyclohexane
1.388	125.0	7.81	0.23	0.92	0.00	0.18	1.00	1.00	0.952	1	1-Hexene
1.383	126.7	7.75	0.23	0.92	0.00	0.18	1.00	1.00	0.952	1	2-Methyl-1-pentene
1.410	112.4	8.05	0.00	1.00	0.00	0.00	1.00	1.00	0.953	1	Methylcyclopentane
1.400	122.6	7.95	0.23	0.92	0.00	0.18	1.00	1.00	0.952	1	2-Methyl-2-pentene
1.396	125.1	7.89	2.42	1.00	0.00	3.00	1.28	1.19	0.896	1	4-Methyl-2-pentanone
1.467	105.4	8.65	0.90	1.00	4.00	4.00	1.19	2.86	0.790	2	Cyclohexanol
1.392	132.0	7.85	2.21	1.00	0.00	2.55	1.22	1.15	0.906	1	Butyl acetate
1.375	130.8	7.67	0.00	1.00	0.00	0.00	1.00	1.00	0.953	1	Hexane
1.375	130.3	7.67	0.00	1.00	0.00	0.00	1.00	1.00	0.953	1	2,3-Dimethylbutane
1.377	129.7	7.68	0.00	1.00	0.00	0.00	1.00	1.00	0.953	1	3-Methylpentane
1.369	132.9	7.60	0.00	1.00	0.00	0.00	1.00	1.00	0.953	1	2,2-Dimethylbutane
1.372	131.9	7.63	0.00	1.00	0.00	0.00	1.00	1.00	0.953	1	2-Methylpentane
1.418	124.7	8.14	0.82	1.00	3.73	3.73	1.17	2.68	0.812	1	Hexanol
1.401	139.0	7.52	0.53	1.00	0.00	4.98	1.00	1.00	0.950	1	Triethylamine
1.528	102.6	8.73	3.30	0.90	0.64	2.94	1.41	1.40	0.829	3	Benzonitrile
1.539	117.2	8.84	2.71	0.90	0.74	0.93	1.26	1.20	0.875	3	Benzyl chloride
1.564	128.4	9.06	2.20	0.90	0.80	3.06	1.17	1.30	0.882	3	Bromoanisole
1.497	106.3	8.45	1.56	0.90	0.15	1.60	1.06	1.04	0.929	3	Toluene
1.517	108.1	8.64	2.77	0.90	0.28	1.60	1.27	1.19	0.874	3	Anisole
1.420	137.2	8.16	2.90	1.00	0.22	1.99	1.45	1.32	0.867	1	Heptanenitrile
1.423	124.4	8.19	0.00	1.00	0.00	0.00	1.00	1.00	0.953	1	Methylcyclohexane
1.400	140.9	7.94	0.24	0.93	0.00	0.22	1.00	1.00	0.952	1	1-Heptene
1.444	121.3	8.40	0.00	1.00	0.00	0.00	1.00	1.00	0.953	2	Cycloheptane
1.406	139.5	8.00	2.17	1.00	0.00	2.69	1.21	1.14	0.907	1	Ethyl butyl ketone
1.388	146.6	7.81	0.00	1.00	0.00	0.00	1.00	1.00	0.953	1	Heptane
1.389	145.8	7.82	0.00	1.00	0.00	0.00	1.00	1.00	0.953	1	3-Methylhexane
1.392	148.7	7.75	0.00	1.00	0.00	0.00	1.00	1.00	0.953	1	2,2-Dimethylpentane
1.381	149.0	7.74	0.00	1.00	0.00	0.00	1.00	1.00	0.953	1	2,4-Dimethylpentane
1.534	116.9	8.79	3.02	0.90	0.86	3.13	1.35	1.45	0.839	3	Acetophenone
1.496	122.5	8.49	1.28	0.90	0.05	0.50	1.03	1.02	0.937	3	Ethylbenzene
1.496	123.3	8.44	1.27	0.90	0.07	0.74	1.03	1.02	0.937	3	p-Xylene
1.506	120.6	8.58	1.65	0.90	0.04	0.90	1.07	1.04	0.926	3	o-Xylene
1.459	134.4	8.56	0.00	1.00	0.00	0.00	1.00	1.00	0.953	2	Cyclooctane
1.409	157.0	8.04	0.23	0.94	0.00	0.21	1.00	1.00	0.952	1	1-Octene
1.433	142.4	8.30	0.00	1.00	0.00	0.00	1.00	1.00	0.953	2	Ethylcyclohexane
1.391	165.1	7.84	0.00	1.00	0.00	0.00	1.00	1.00	0.953	1	Isooctane
1.397	162.6	7.91	0.00	1.00	0.00	0.00	1.00	1.00	0.953	1	Octane
1.430	157.8	8.26	0.69	1.00	3.13	3.13	1.12	2.22	0.854	1	Octanol
1.627	118.1	9.60	2.80	0.90	0.34	3.10	1.28	1.24	0.867	3	Quinoline
1.527	132.9	8.73	2.74	0.90	0.69	2.91	1.28	1.33	0.861	3	Propiophenone
1.523	142.4	8.69	3.26	0.90	0.23	2.51	1.38	1.28	0.845	3	Benzyl acetate
1.427	163.8	8.23	0.00	1.00	0.00	0.00	1.00	1.00	0.953	2	1,3,5-Trimethylcyclohexane
1.420	173.1	8.15	1.78	1.00	0.00	2.21	1.12	1.08	0.922	1	Dibutyl ketone
1.412	176.6	8.07	1.60	1.00	0.00	2.40	1.09	1.06	0.928	1	Diisobutyl ketone
1.405	178.7	8.00	0.00	1.00	0.00	0.00	1.00	1.00	0.953	1	Nonane
1.418	189.6	7.63	0.45	1.00	0.00	3.30	1.00	1.00	0.951	1	Tripropylamine
1.658	139.6	9.85	1.95	0.90	0.57	0.38	1.11	1.08	0.914	3	Bromonaphthalene
1.490	156.0	8.43	1.00	0.90	0.05	0.40	1.02	1.01	0.943	3	Butylbenzene
1.481	154.0	8.80	0.00	1.00	0.00	0.00	1.00	1.00	0.953	3	Decalin
1.430	186.9	8.26	2.27	1.00	0.17	1.56	1.24	1.17	0.901	1	Decanenitrile
1.441	175.5	8.38	0.00	1.00	0.00	0.00	1.00	1.00	0.953	2	Butyl cyclohexane
1.421	189.3	8.17	0.21	0.95	0.00	0.19	1.00	1.00	0.953	1	1-Decene
1.506	143.6	9.05	1.56	1.00	0.00	1.81	1.08	1.06	0.929	1	Ethyloctanoate
1.412	194.9	8.07	0.00	1.00	0.00	0.00	1.00	1.00	0.953	1	Decane
1.437	190.8	8.34	0.60	1.00	2.72	2.72	1.09	1.89	0.878	1	Decanol
1.422	227.5	8.17	0.00	1.00	0.00	0.00	1.00	1.00	0.953	1	Dodecane
1.445	286.0	8.42	1.62	1.00	0.12	1.11	1.10	1.07	0.926	1	Palmitanitrile
1.441	287.3	8.38	0.10	0.97	0.00	0.11	1.00	1.00	0.953	1	Hexadecene
1.451	301.5	8.49	0.72	1.00	0.11	0.07	1.01	1.01	0.948	1	n-Hexadecyl chloride
1.462	305.6	8.60	0.66	1.00	0.10	0.07	1.01	1.00	0.949	1	n-Hexadecyl bromide
1.435	292.8	8.32	0.00	1.00	0.00	0.00	1.00	1.00	0.953	1	Hexadecane
1.449	288.0	8.47	0.44	1.00	1.99	1.99	1.05	1.40	0.913	1	Hexadecanol

TABLE 8-19   Parameters for MOSCED Model at 20°C   (*Continued*)

RI	v	λ	τ	q	α	β	ψ	ξ	aa	ID	Compound
1.439	327.1	8.36	0.00	1.00	0.00	0.00	1.00	1.00	0.953	1	Octadecane
1.443	358.3	8.40	0.00	1.00	0.00	0.00	1.00	1.00	0.953	1	Eicosane
1.444	374.6	8.41	0.00	1.00	0.00	0.00	1.00	1.00	0.953	1	Heneicosane
1.448	423.8	8.45	0.00	1.00	0.00	0.00	1.00	1.00	0.953	1	Tetracosane
1.452	489.4	8.50	0.00	1.00	0.00	0.00	1.00	1.00	0.953	1	Octacosane
1.499	478.5	8.98	0.28	0.87	0.00	0.70	1.00	1.00	0.952	1	Squalene
1.454	522.2	8.51	0.00	1.00	0.00	0.00	1.00	1.00	0.953	1	Triacontane
1.453	522.0	8.50	0.00	1.00	0.00	0.00	1.00	1.00	0.953	1	Squalane
1.455	555.0	8.53	0.00	1.00	0.00	0.00	1.00	1.00	0.953	1	Dotriacontane
1.457	604.4	8.55	0.00	1.00	0.00	0.00	1.00	1.00	0.953	1	Pentatriacontane

Parameters τ, α, β, ψ, ξ, and aa are temperature-dependent. The temperature dependence is given by

$$\tau_T = \tau_{293} \left(\frac{293}{T} \right)^{0.4} \tag{8-10.29}$$

$$\alpha_T = \alpha_{293} \left(\frac{293}{T} \right)^{0.8} \qquad \beta_T = \beta_{293} \left(\frac{293}{T} \right)^{0.8} \tag{8-10.30}$$

$$\psi = \text{POL} + 0.011 \alpha_T \beta_T \tag{8-10.31}$$

$$\xi = 0.68(\text{POL} - 1) + \{3.4 - 2.4 \exp[(-0.023)(\alpha_0 \beta_0)^{1.5}]\}^{t^2} \tag{8-10.32}$$

where

$$\text{POL} = q^4[1.15 - 1.15 \exp(-0.020\tau_T^3)] + 1 \tag{8-10.33}$$

and where $t = 293/T$ (T in kelvins). Subscript 0 refers to 20°C (293 K), and subscript T refers to system temperature.

$$aa = 0.953 - 0.00968(\tau_2^2 + \alpha_2 \beta_2) \tag{8-10.34}$$

where τ, α, and β are at system temperature T.

In Eq. (8-10.27), when subscripts 1 and 2 are interchanged, there is no effect in the terms $(\lambda_1 - \lambda_2)^2$, $q_1^2 q_2^2 (\tau_1 - \tau_2)^2$, and $(\alpha_1 - \alpha_2)(\beta_1 - \beta_2)$. Asymmetry is introduced through parameters ψ and ξ because $\psi_1 \neq \psi_2$ and $\xi_1 \neq \xi_2$.

In Table 8-19, RI refers to refractive index and ID refers to identification number. ID = 1 for alkane, 2 for naphthene, and 3 for aromatic.

The units of the parameters in Table 8-19 are such that, in the equation for $\ln \gamma_2^\infty$, gas constant R has the value 1.987 cal/mol·K.

For substances not listed in the table, parameters for some classes of compounds can be estimated by the following equations:

Dispersion parameter
Nonaromatics:†

$$\lambda = 10.3 \frac{n_D^2 - 1}{n_D^2 + 2} + 3.02 \tag{8-10.35}$$

---

†Except for tertiary amines, nitriles, and CS_2.

Aromatics:

$$\lambda = 19.5 \frac{n_D^2 - 1}{n_D^2 + 2} + 2.79 \tag{8-10.36}$$

$n_D \equiv$ refractive index for the sodium D line.

Induction parameter

$q = 1.0$ for saturated compounds

$q = 0.9$ for aromatics

$q = 1.0 - 0.5$ [(No. C=C bonds)/(No. C atoms)] for unsaturated aliphatics

Polar and acidity and basicity parameters†

$$\tau, \alpha, \beta = C_{(\tau,\alpha,\beta)} \left(\frac{4.5}{3.5 + \text{No. C}} \right) \left(1 + \frac{\text{No. C} - 1}{100} \right) \tag{8-10.37}$$

where the constants are as tabulated.

	C_τ	C_α	C_β		C_τ	C_α	C_β
Chlorides	2.69	0.42	0.25	Nitroalkanes	5.87	0.35	2.66
Bromides	2.47	0.39	0.38	Alcohols	1.65	7.49	7.49
Iodides	2.02	0.37	0.30	Esters	4.03	0.00	4.64†
Nitriles	5.84	0.33	4.00	Ketones	3.93	0.00	4.87‡

†No. C atoms = 1 for methylformate.

‡No. C atoms = 1 for acetone.

Constants C_τ, C_α, and C_β are restricted to monofunctional, primary alkanes. Not enough information is available to predict the effects of multifunctionalities, secondary or tertiary positioning of the functional group, chain branching, and cyclic or aromatic backbones.

Like any model for mixture properties, MOSCED has both advantages and disadvantages:

Advantages

1. Good overall quantitative predictions. For 3357 γ^∞'s, an average error of 9.1 percent was achieved with few errors greater than 30 percent. This compares with an average error of 20.5 percent with UNIFAC.‡

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†Except for first member of a homologous series and for ethanol.

‡While UNIFAC is often in error at high dilution, it is usually reliable at intermediate mole fractions.

2. Parameters have some physical significance which give a "feel" for the relative magnitudes of the types of forces in a solution.

3. Calculations are tedious but simple.

4. The model applies to a large number of binary mixtures.

Disadvantages

1. Since numerous modifications were made to adjust pure component parameters (e.g., molar volumes of aniline, CS_2, and iodides and the λ's of nitriles, tertiary amines, and CS_2), the general applicability of the model is limited.

2. Predictions are poor for systems where steric considerations are significant, e.g., systems containing TEA (triethylamine) with a moderate or strong acid.

3. Cannot be used for aqueous systems.

4. Works only for systems with activity coefficients below about 100.

Example 8-8 Calculate the P-y-x diagram at 50.2°C for the system cyclohexane (1)–aniline (2).

solution From the MOSCED model, limiting activity coefficients (γ^∞'s) are predicted for the system. To calculate the diagram over the entire composition range, binary parameters are obtained from a model for the excess Gibbs energy by using γ_1^∞ and γ_2^∞ to fix parameters. MOSCED parameters at 20°C are taken from Table 8-19:

	Cyclohexane (1)	Aniline (2)		Cyclohexane (1)	Aniline (2)
υ	108.1	91.1	β	0	2.13
λ	8.22	9.25	ψ	1	1.68
τ	0	4.22	ξ	1	2.39
q	1	0.90	aa	0.953	0.702
α	0	3.81			

τ, α, β, ψ, ξ, and aa are temperature-dependent. For aniline, these parameters at 50.2°C (323.2 K) are obtained from

$$\tau_{323.2} = (4.22)\left(\frac{293}{323.2}\right)^{0.4} = 4.06$$

$$\alpha_{323.2} = (3.81)\left(\frac{293}{323.2}\right)^{0.8} = 3.52$$

$$\beta_{323.2} = (2.13)\left(\frac{293}{323.2}\right)^{0.8} = 1.97$$

$$\text{POL} = 0.9^4\{1.15 - 1.15 \exp[(-0.020)(4.06)^3]\} + 1 = 1.557$$

$$\psi_{323.2} = 1.557 + (0.011)(3.52)(1.97) = 1.63$$

$$\xi_{323.2} = (0.68)(1.557 - 1) + [3.4 - 2.4 \exp\{(-0.023)[(3.81)(2.13)]^{1.5}\}]^{(293/323.2)^2}$$

$$= 2.14$$

$$aa_{323.2} = 0.953 - (0.00968)[4.06^2 + (3.52)(1.97)] = 0.726$$

The temperature-dependent parameters are obtained similarly for cyclohexane. Summarizing,

	Cyclohexane (1)	Aniline (2)		Cyclohexane (1)	Aniline (2)
v	108.1	91.1	β	0	1.97
λ	8.22	9.25	ψ	1	1.63
τ	0	4.06	ξ	1	2.14
q	1	0.9	aa	0.953	0.726
α	0	3.52			

Next, we calculate the combinatorial term:

$$d_{12} = \ln\left(\frac{91.1}{108.1}\right)^{0.726} + 1 - \left(\frac{91.1}{108.1}\right)^{0.726} = -0.00741$$

$$d_{12} = \ln\left(\frac{108.1}{91.1}\right)^{0.953} + 1 - \left(\frac{108.1}{91.1}\right)^{0.953} = -0.01405$$

Finally, we calculate the infinite dilution activity coefficients:

$$\gamma_1^\infty = \exp\left\{\frac{108.1}{(1.987)(323.2)}\left[(9.25 - 8.22)^2 + \frac{(0.9)^2(4.06)^2}{1.63} + \frac{(3.52)(1.97)}{2.14}\right] - 0.01405\right\} = 8.08$$

$$\gamma_2^\infty = \exp\left\{\frac{91.1}{(1.987)(323.2)}\left[(8.22 - 9.25)^2 + \frac{(0.9)^2(4.06)^2}{1.0} + \frac{(3.52)(1.97)}{1.0}\right] - 0.00741\right\}$$

$$= 20.5$$

We choose the Wilson equation for excess Gibbs energy. We find binary parameters Λ_{12} and Λ_{21} from Eqs. (8-10.25) and (8-10.26). By solving those equations simultaneously, we obtain

$$\Lambda_{12} = 0.3051 \qquad \Lambda_{21}: 0.09773$$

We can now calculate the P-y-x diagram. In view of the approximate nature of this calculation, we neglect all vapor phase corrections and the Poynting factor. Recall that

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right)$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) - x_1\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right)$$

$$P = \gamma_1 x_1 P_{vp1} + \gamma_2 x_2 P_{vp2}$$

$$y_i = \frac{\gamma_i x_i P_{vpi}}{P}$$

where P_{vpi} is the pure component vapor pressure at temperature T. At 50.2°C, $P_{vp1} = 0.3604$ bar and $P_{vp2} = 0.00493$ bar.
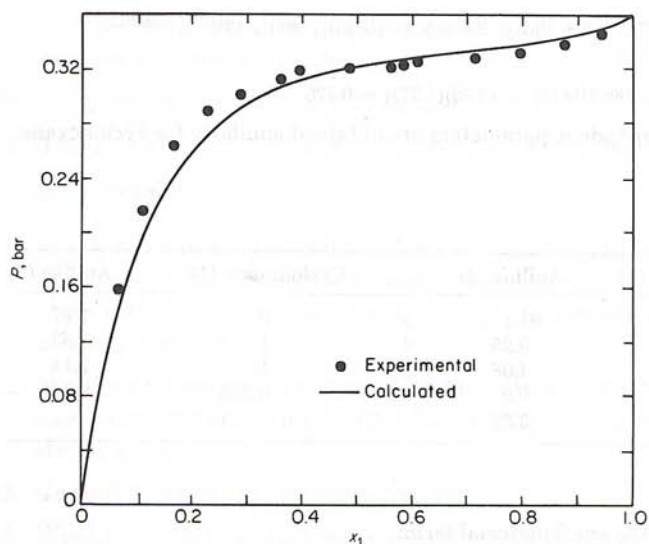
Figure 8-10 Calculated and experimental total pressures for the system cyclohexane (1)–aniline (2) at 50.2°C. Activity coefficients calculated from Wilson equation with parameters determined from MOSCED correlation for infinite-dilution activity coefficients.

The results are summarized in the accompanying table and Fig. 8-10. The experimental data are taken from Abello et al. [1].

Vapor-Liquid Equilibrium Composition for Cyclohexane (1)–Aniline (2) at 50.2°C

	$100y_1$			$100y_1$	
$100x_1$	Calculated	Observed	$100x_1$	Calculated	Observed
6.4	96.7	97.2	48.6	98.8	98.9
10.9	97.7	97.9	58.2	98.8	98.9
16.8	98.2	98.4	71.3	98.9	98.8
28.4	98.6	98.8	87.4	99.0	99.1
36.0	98.7	98.8	93.9	99.2	99.3

Example 8-9 Repeat the preceding example for the system methanol (1)–benzene (2) at 35°C.

solution At 20°C, the MOSCED parameters are:

Parameter	Methanol	Benzene	Parameter	Methanol	Benzene
v	40.5	89.1	β	7.45	0.56
λ	7.14	8.49	Ψ	1.94	1.11
τ	2.55	1.95	ξ	3.62	1.07
q	1	0.9	aa	0.353	0.915
α	7.45	0.22			

As in the preceding example, the parameters at 35°C are calculated. Summarizing,

Parameter	Methanol	Benzene	Parameter	Methanol	Benzene
v	40.5	89.1	β	7.16	0.538
λ	7.14	8.49	Ψ	1.87	1.10
τ	2.50	1.91	ξ	3.24	1.07
q	1	0.9	aa	0.396	0.916
α	7.16	0.211			

The combinatorial terms are given by

$$d_{12} = \ln \left(\frac{89.1}{40.5}\right)^{0.916} + 1 - \left(\frac{89.1}{40.5}\right)^{0.916} = -0.337$$

$$d_{21} = \ln \left(\frac{40.5}{89.1}\right)^{0.396} + 1 - \left(\frac{40.5}{89.1}\right)^{0.396} = -0.0440$$

Finally, we calculate the infinite-dilution activity coefficients:

$$\gamma_1^\infty = \exp \left\{ \frac{40.5}{(1.987)(308)} \left[(8.49 - 7.14)^2 + \frac{(0.9)^2(1.91 - 2.50)^2}{1.10} \right. \right.$$

$$\left. \left. + \frac{(0.211 - 7.16)(0.538 - 7.16)}{1.07} \right] - 0.0440 \right\}$$

$$= 18.9$$

$$\gamma_2^\infty = \exp \left\{ \frac{89.1}{(1.987)(308)} \left[(7.14 - 8.49)^2 + \frac{(0.9)^2(2.50 - 1.91)^2}{1.87} \right. \right.$$

$$\left. \left. + \frac{(7.16 - 0.211)(7.16 - 0.538)}{3.24} \right] - 0.337 \right\}$$

$$= 7.52$$

For the Wilson equation, using γ_1^∞ and γ_2^∞, the binary parameters are

$$\Lambda_{12} = 0.1038 \qquad \Lambda_{21} = 0.3258$$

At 35°C, $P_{vp1} = 0.2759$ bar and $P_{vp2} = 0.1952$ bar

The results are shown in Fig. 8-11. Experimental data are taken from Scatchard et al. [108].

Azeotropic data

Many binary systems exhibit azeotropy, i.e., a condition in which the composition of a liquid mixture is equal to that of its equilibrium vapor. When the azeotropic conditions (temperature, pressure, composition) are known, activity coefficients γ_1 and γ_2 at that condition are readily found. These activity coefficients can then be used to calculate two parameters in some arbitrarily chosen expression for the excess Gibbs energy (Table 8-3). Extensive compilations of azeotropic data are available [56].
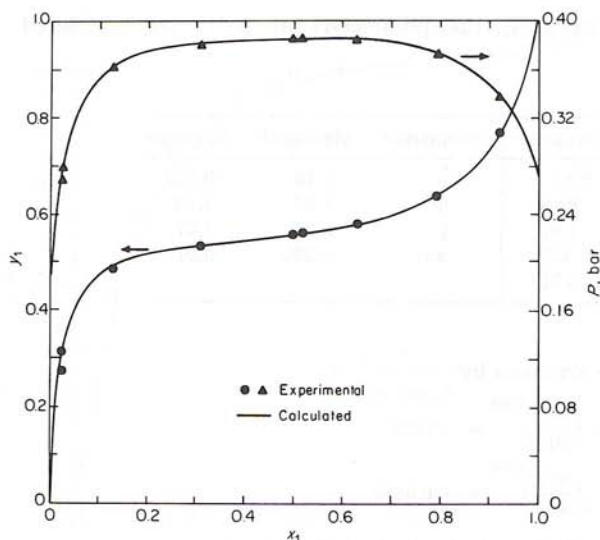
Figure 8-11 Calculated and observed vapor-liquid equilibria for methanol (1)–benzene (2) at 35°C. Activity coefficients calculated from the Wilson equation with parameters determined from the MOSCED correlation for infinite-dilution activity coefficients.

For a binary azeotrope, $x_1 = y_1$ and $x_2 = y_2$. Therefore, Eq. (8-4.1), with $\mathcal{F}_i = 1$, becomes

$$\gamma_1 = \frac{P}{P_{vp1}} \quad \text{and} \quad \gamma_2 = \frac{P}{P_{vp2}} \tag{8-10.38}$$

Knowing total pressure P and pure component vapor pressures P_{vp1} and P_{vp2}, we determine γ_1 and γ_2. With these activity coefficients and the azeotropic composition x_1 and x_2 it is now possible to find two parameters A and B by simultaneous solution of two equations of the form

$$RT \ln \gamma_1 = f_1(x_2, A, B) \tag{8-10.39a}$$
$$RT \ln \gamma_2 = f_2(x_1, A, B) \tag{8-10.39b}$$

where, necessarily, $x_1 = 1 - x_2$ and where functions f_1 and f_2 represent thermodynamically consistent equations derived from the choice of an expression for the excess Gibbs energy. Simultaneous solution of Eqs. (8-10.39a) and (8-10.39b) is simple in principle, although the necessary algebra may be tedious if f_1 and f_2 are complex.

Example 8-10 To illustrate, consider an example similar to one given by Treybal [123] for the system ethyl acetate (1)–ethanol (2). This system forms an azeotrope at 1.01 bar, 71.8°C, and $x_2 = 0.462$.

solution   At 1.01 bar and 71.8°C, we use Eq. (8-10.38):

$$\gamma_1 = \frac{1.01}{0.839} = 1.204 \qquad \gamma_2 = \frac{1.01}{0.772} = 1.308$$

where 0.839 and 0.772 bar are the pure component vapor pressures at 71.8°C. For functions f_1 and f_2 we choose the van Laar equations shown in Table 8-3. Upon algebraic rearrangement, we obtain explicit solutions for A and B.

$$\frac{A}{RT} = \ln 1.204 \left(1 + \frac{0.462 \ln 1.308}{0.538 \ln 1.204}\right)^2 = 0.93$$

$$\frac{B}{RT} = \ln 1.308 \left(1 + \frac{0.538 \ln 1.204}{0.462 \ln 1.308}\right)^2 = 0.87$$

and $A/B = 1.07$.

At 71.8°C, the activity coefficients are given by

$$\ln \gamma_1 = \frac{0.93}{(1 + 1.07 x_1/x_2)^2}$$

$$\ln \gamma_2 = \frac{0.87}{(1 + x_2/1.07 x_1)^2}$$

Figure 8-12 shows a plot of the calculated activity coefficients. Also shown are experimental results at 1.01 bar by Furnas and Leighton [39] and by Griswold, Chu, and Winsauer [43]. Since the experimental results are isobaric, the temperature is not constant. However, in this example, the calculated activity coefficients are assumed to be independent of temperature.

Figure 8-12 shows good overall agreement between experimental and calculated activity coefficients. Generally, fair agreement is found if the azeotropic data are accurate, if the binary system is not highly complex, and, most important, if the azeotropic composition is in the midrange $0.25 < x_1$ (or x_2) < 0.75. If the azeotropic composition is at either dilute end, azeotropic data are of much less value for estimating activity coefficients over the entire composition range. This negative conclusion follows from the limiting relation $\gamma_1 \rightarrow 1$ as $x_1 \rightarrow 1$. Thus, if we have an azeotropic mixture where $x_2 \ll 1$, the experimental value of γ_1 gives us very little information, since γ_1 is necessarily close to unity. For such a mixture, only γ_2 supplies significant information, and therefore we cannot expect to calculate two meaningful adjustable parameters when we have only one significant datum. However, if the azeotropic composition is close to unity, we may, nevertheless, use the azeotropic data to find one activity coefficient, namely, γ_2 (where $x_2 \ll 1$), and then use that γ_2 to determine the single adjustable parameter in any of the one-parameter equations for the molar excess Gibbs energy, as discussed in Sec. 8-5.

Mutual solubilities of liquids

When two liquids are only partially miscible, experimental data for the two mutual solubilities can be used to estimate activity coefficients over
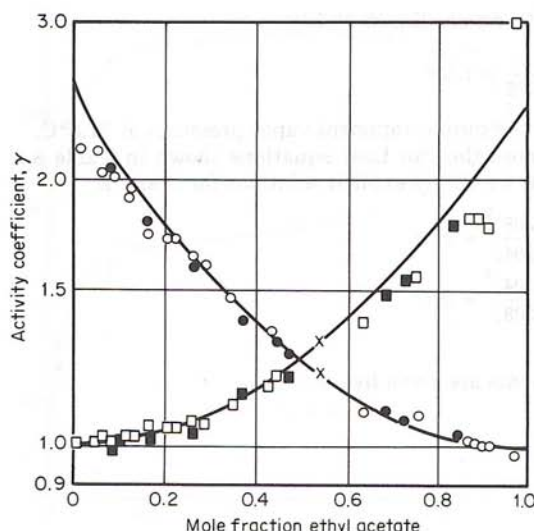
Figure 8-12 Activity coefficients in the system ethyla-cetate–ethanol. Calculated lines from azeotropic data (indicated by x) at 1.01 bar. Points are experimental [39, 43]. *(From Ref. 123.)*

the entire range of composition in the homogeneous regions. Suppose the solubility (mole fraction) of component 1 in component 2 is $x_1^{s'}$ and that of component 2 in component 1 is $x_2^{s''}$, where superscript s denotes saturation and the primes designate the two liquid phases. If $x_1^{s'}$ and $x_2^{s''}$ are known at some temperature T, it is possible to estimate acitivity coefficients for both components in the homogeneous regions $0 \leqslant x_1' \leqslant x_1^{s'}$ and $0 \leqslant x_2'' \leqslant x_2^{s''}$.

To estimate the activity coefficients, it is necessary to choose some thermodynamically consistent analytical expression which relates activity coefficients γ_1 and γ_2 to mole fraction x. (See Sec. 8-5.) Such an expression contains one or more constants characteristic of the binary system; these constants are generally temperature-dependent, although the effect of temperature is often not large. From the equations of liquid-liquid equilibrium, it is possible to determine two of these constants. The equations of equilibrium are

$$(\gamma_1 x_1)^{s'} = (\gamma_1 x_1)^{s''} \quad \text{and} \quad (\gamma_2 x_2)^{s'} = (\gamma_2 x_2)^{s''} \qquad (8\text{-}10.40)$$

Suppose we choose a two-constant expression for the molar excess Gibbs energy g^E. Then, as discussed in Sec. 8-5,

$$RT \ln \gamma_1 = f_1(x_2, A, B) \quad \text{and} \quad RT \ln \gamma_2 = f_2(x_1, A, B) \qquad (8\text{-}10.41)$$

where f_1 and f_2 are known functions and the two (unknown) constants are designated by A and B. These constants can be found by simultaneous

solution of Eqs. (8-10.40) and (8-10.41) coupled with experimental values for $x_1^{s'}$ and $x_2^{s''}$ and the material balances

$$x_2^{s'} = 1 - x_1^{s'} \quad \text{and} \quad x_1^{s''} = 1 - x_2^{s''} \tag{8-10.42}$$

In principle, the calculation is simple although the algebra may be tedious, depending on the complexity of the functions f_1 and f_2.

To illustrate, Table 8-20 presents results obtained by Brian [21] for five binary aqueous systems, where subscript 2 refers to water. Calculations are based on both the van Laar equation and the three-suffix (two-parameter) Margules equation (see Table 8-3). Table 8-20 shows the calculated activity coefficients at infinite dilution, which are easily related to the constants A and B. [See Eqs. (8-10.23) and (8-10.24).]

Brian's calculations indicate that results are sensitive to the expression arbitrarily chosen for the molar excess Gibbs energy. Brian found that, compared with experimental vapor-liquid equilibrium data for the homogeneous regions, the Margules equations gave poor results and the van Laar equation gave fair, but not highly accurate, results.

Calculations of this sort can also be made by using a three-parameter equation for g^E, but in that event, the third parameter must be estimated independently. A nomogram for such calculations, using the NRTL equation, has been given by Renon and Prausnitz [105].

Generally speaking, mutual solubility data provide only approximate values of activity coefficients, although such estimates may be better than none at all. These estimates are sensitive not only to the choice of an expression for g^E but also to small errors in the experimental mutual solubility data.

Group contribution methods

For correlating thermodynamic properties, it is often convenient to regard a molecule as an aggregate of functional groups; as a result, some thermodynamic properties of pure fluids, e.g., heat capacity and critical vol-

TABLE 8-20 Limiting Activity Coefficients as Calculated from Mutual Solubilities in Five Binary Aqueous Systems [21]

Component (1)	Temp., °C	Solubility limits		$\log \gamma_1^\infty$		$\log \gamma_2^\infty$	
		x_1''	x_2'	van Laar	Margules	van Laar	Margules
Aniline	100	0.01475	0.372	1.8337	1.5996	0.6076	−0.4514
Isobutyl alcohol	90	0.0213	0.5975	1.6531	0.6193	0.4020	−3.0478
1-Butanol	90	0.0207	0.636	1.6477	0.2446	0.3672	−4.1104
Phenol	43.4	0.02105	0.7325	1.6028	−0.1408	0.2872	−8.2901
Propylene oxide	36.3	0.166	0.375	1.1103	1.0743	0.7763	0.7046

ume, can be calculated by summing group contributions. Extension of this concept to mixtures was suggested long ago by Langmuir, and several attempts have been made to establish group contribution methods for heats of mixing and for activity coefficients. Here we mention only two methods, both for activity coefficients, which appear to be particularly useful for making reasonable estimates for those strongly nonideal mixtures for which data are sparse or totally absent. The two methods, called ASOG and UNIFAC, are similar in principle but differ in detail.

In any group contribution method, the basic idea is that whereas there are thousands of chemical compounds of interest in chemical technology, the number of functional groups which constitute these compounds is much smaller. Therefore, if we assume that a physical property of a fluid is the sum of contributions made by the molecule's functional groups, we obtain a possible technique for correlating the properties of a very large number of fluids in terms of a much smaller number of parameters which characterize the contributions of individual groups.

Any group contribution method is necessarily approximate because the contribution of a given group in one molecule is not necessarily the same as that in another molecule. The fundamental assumption of a group contribution method is additivity: the contribution made by one group within a molecule is assumed to be independent of that made by any other group in that molecule. This assumption is valid only when the influence of any one group in a molecule is not affected by the nature of other groups within that molecule.

For example, we would not expect the contribution of a carbonyl group in a ketone (say, acetone) to be the same as that of a carbonyl group in an organic acid (say, acetic acid). On the other hand, experience suggests that the contribution of a carbonyl group in, for example, acetone, is close to (although not identical with) the contribution of a carbonyl group in another ketone, say 2-butanone.

Accuracy of correlation improves with increasing distinction of groups; in considering, for example, aliphatic alcohols, in a first approximation no distinction is made between the position (primary or secondary) of a hydroxyl group, but in a second approximation such a distinction is desirable. In the limit, as more and more distinctions are made, we recover the ultimate group, namely, the molecule itself. In that event, the advantage of the group contribution method is lost. For practical utility, a compromise must be attained. The number of distinct groups must remain small but not so small as to neglect significant effects of molecular structure on physical properties.

Extension of the group contribution idea to mixtures is attractive because, although the number of pure fluids in chemical technology is already very large, the number of different mixtures is larger by many orders of magnitude. Thousands, perhaps millions, of multicomponent

liquid mixtures of interest in the chemical industry can be constituted from perhaps 30, 50, or at most 100 functional groups.

ASOG method

The analytical solution of groups (ASOG) method was developed by Wilson and Deal [131] and Wilson [130] following earlier work by Redlich, Derr, Pierotti, and Papadopoulos [104]. An introduction to ASOG was presented by Palmer [87].

For component i in a mixture, activity coefficient γ_i consists of a configurational (entropic) contribution due to differences in molecular size and a group interaction contribution due primarily to differences in intermolecular forces:

$$\ln \gamma_i = \ln \gamma_i^S + \ln \gamma_i^G \tag{8-10.43}$$

where superscript S designates size and superscript G designates group.

Activity coefficient γ_i^S depends only on the number of size groups, e.g., CH_2, CO, OH, in the various molecules that constitute the mixture. From the Flory-Huggins theory for athermal mixtures of unequal-size molecules:

$$\ln \gamma_i^S = 1 - \mathcal{R}_i + \ln \mathcal{R}_i \tag{8-10.44}$$

$$\text{where} \qquad \mathcal{R}_i = \frac{s_i}{\sum_j s_j x_j} \tag{8-10.45}$$

where x_j = mole fraction of component j in mixture
$\quad\;\; s_j$ = number of size groups in molecule j

Parameter s_j is independent of temperature. The summation extends over all components, including component i.

To calculate γ_i^G, we need to know the *group* mole fractions X_k, where subscript k stands for a particular group in molecule j

$$X_k = \frac{\sum_j x_j \nu_{kj}}{\sum_j x_j \sum_k \nu_{kj}} \tag{8-10.46}$$

where ν_{kj} is the number of interaction groups k in molecule j. Activity coefficient γ_i^G is given by

$$\ln \gamma_i^G = \sum_k \nu_{ki} \ln \Gamma_k - \sum_k \nu_{ki} \ln \Gamma_k^* \tag{8-10.47}$$

where Γ_k = activity coefficient of group k in the mixture
$\quad\;\; \Gamma_k^*$ = activity coefficient of group k in the standard state

This standard state depends on molecule i.

Activity coefficient Γ_k is given by Wilson's equation

$$\ln \Gamma_k = -\ln \sum_\ell X_\ell A_{k\ell} + \left(1 - \sum_\ell \frac{X_\ell A_{\ell k}}{\sum_m x_m A_{\ell m}}\right) \qquad \text{(8-10.48)}$$

where the summations extend over all groups present in the mixture.

Equation (8-10.48) is also used to find Γ_k^* for component i, but in that case it is applied to a "mixture" of groups as found in pure component i. For example, if i is water, hexane,† or benzene, there is only one kind of group and $\ln \Gamma_k^*$ is zero. However, if i is methanol, $\ln \Gamma_k^*$ has a finite value for both hydroxyl and methyl groups.

Parameters $A_{k\ell}$ and $A_{\ell k}$ $(A_{k\ell} \neq A_{\ell k})$ are group interaction parameters which depend on temperature. These parameters are obtained from reduction of vapor-liquid equilibria, and a substantial number of such parameters have been reported by Derr and Deal [30] and by Kojima and Tochigi [62a]. The important point here is that, at a fixed temperature, these parameters depend only on the nature of the groups and, by assumption, are independent of the nature of the molecule. Therefore, group parameters obtained from available experimental data for some mixtures can be used to predict activity coefficients in other mixtures that contain not the same molecules, but the same groups. For example, suppose we wish to predict activity coefficients in the binary system dibutyl ketone–nitrobenzene. To do so, we require group interaction parameters for characterizing interactions between methyl, phenyl, keto, and nitrile groups. These parameters can be obtained from other binary mixtures which contain these groups, e.g., acetone-benzene, nitropropane-toluene, and methyl ethyl ketonenitro–ethane.

UNIFAC method

The fundamental idea of a solution-of-groups model is to utilize existing phase equilibrium data for predicting phase equilibria of systems for which no experimental data are available. In concept, the UNIFAC method follows the ASOG method, wherein activity coefficients in mixtures are related to interactions between structural groups. The essential features are:

1. Suitable reduction of experimentally obtained activity coefficient data to yield parameters characterizing interactions between pairs of structural groups in nonelectrolyte systems.

2. Use of those parameters to predict activity coefficients for other sys-

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†It is assumed here that with respect to group interactions, no distinction is made between groups CH_2 and CH_3.

tems which have not been studied experimentally but which contain the same functional groups.

The molecular activity coefficient is separated into two parts: one part provides the contribution due to differences in molecular size, and the other provides the contribution due to molecular interactions. In ASOG, the first part is arbitrarily estimated by using the athermal Flory-Huggins equation; the Wilson equation, applied to functional groups, is chosen to estimate the second part. Some of this arbitrariness is removed by combining the solution-of-groups concept with the UNIQUAC equation (see Table 8-3); first, the UNIQUAC model per se contains a combinatorial part, essentially due to differences in size and shape of the molecules in the mixture, and a residual part, essentially due to energy interactions, and second, functional group sizes and interaction surface areas are introduced from independently obtained, pure component molecular structure data.

The UNIQUAC equation often gives good representation of both vapor-liquid and liquid-liquid equilibria for binary and multicomponent mixtures containing a variety of nonelectrolytes such as hydrocarbons, ketones, esters, water, amines, alcohols, nitriles, etc. In a multicomponent mixture, the UNIQUAC equation for the activity coefficient of (molecular) component i is

$$\ln \gamma_i = \underset{\text{combinatorial}}{\ln \gamma_i^C} + \underset{\text{residual}}{\ln \gamma_i^R} \tag{8-10.49}$$

where

$$\ln \gamma_i^C = \ln \frac{\Phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\Phi_i} + \ell_i - \frac{\Phi_i}{x_i} \sum_j x_j \ell_j \tag{8-10.50}$$

and

$$\ln \gamma_i^R = q_i \left[1 - \ln \left(\sum_j \theta_j \tau_{ji} \right) - \sum_j \frac{\theta_j \tau_{ij}}{\sum_k \theta_k \tau_{kj}} \right] \tag{8-10.51}$$

$$\ell_i = \frac{z}{2} (r_i - q_i) - (r_i - 1) \qquad z = 10$$

$$\theta_i = \frac{q_i x_i}{\sum_j q_j x_j} \qquad \Phi_i = \frac{r_i x_i}{\sum_j r_j x_j} \qquad \tau_{ji} = \exp \left(-\frac{u_{ji} - u_{ii}}{RT} \right)$$

In these equations x_i is the mole fraction of component i and the summations in Eqs. (8-10.50) and (8-10.51) are over all components, including component i, θ_i is the area fraction, and Φ_i is the segment fraction, which is similar to the volume fraction. Pure component parameters r_i and q_i are, respectively, measures of molecular van der Waals volumes and molecular surface areas.

In UNIQUAC, the two adjustable binary parameters τ_{ij} and τ_{ji} appearing in Eq. (8-10.51) must be evaluated from experimental phase equilib-

rium data. No ternary (or higher) parameters are required for systems containing three or more components.

In the UNIFAC method [36], the combinatorial part of the UNIQUAC activity coefficients, Eq. (8-10.50), is used directly. Only pure component properties enter into this equation. Parameters r_i and q_i are calculated as the sum of the group volume and area parameters R_k and Q_k, given in Table 8-21:

$$r_i = \sum_k \nu_k^{(i)} R_k \quad \text{and} \quad q_i = \sum_k \nu_k^{(i)} Q_k \tag{8-10.52}$$

where $\nu_k^{(i)}$, always an integer, is the number of groups of type k in molecule i. Group parameters R_k and Q_k are obtained from the van der Waals group volume and surface areas V_{wk} and A_{wk}, given by Bondi [16]:

$$R_k = \frac{V_{wk}}{15.17} \quad \text{and} \quad Q_k = \frac{A_{wk}}{2.5 \times 10^9} \tag{8-10.53}$$

The normalization factors 15.17 and 2.5×10^9 are determined by the volume and external surface area of a CH_2 unit in polyethylene.

The residual part of the activity coefficient, Eq. (8-10.51), is replaced by the solution-of-groups concept. Instead of Eq. (8-10.51), we write

$$\ln \gamma_i^R = \sum_{\substack{k \\ \text{all groups}}} \nu_k^{(i)}(\ln \Gamma_k - \ln \Gamma_k^{(i)}) \tag{8-10.54}$$

where Γ_k is the group residual activity coefficient and $\Gamma_k^{(i)}$ is the residual activity coefficient of group k in a reference solution containing only molecules of type i. (In UNIFAC, $\Gamma^{(i)}$ is similar to ASOG's Γ^*.) In Eq. (8-10.54) the term $\ln \Gamma_k^{(i)}$ is necessary to attain the normalization that activity coefficient γ_i becomes unity as $x_i \to 1$. The activity coefficient for group k in molecule i depends on the molecule i in which k is situated. For example, $\Gamma_k^{(i)}$ for the COH group† in ethanol refers to a "solution" containing 50 group percent COH and 50 group percent CH_3 at the temperature of the mixture, whereas $\Gamma_k^{(i)}$ for the COH group in n-butanol refers to a "solution" containing 25 group percent COH, 50 group percent CH_2, and 25 group percent CH_3.

The group activity coefficient Γ_k is found from an expression similar to Eq. (8-10.51):

$$\ln \Gamma_k = Q_k \left[1 - \ln \left(\sum_m \theta_m \Psi_{mk} \right) - \sum_m \frac{\theta_m \Psi_{km}}{\sum_n \theta_n \Psi_{nm}} \right] \tag{8-10.55}$$

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†COH is shortened notation for CH_2OH.

TABLE 8-21 UNIFAC Group Specifications and Sample Group Assignments

Group numbers		Name	R	Q	MW
Main	Sec.				
1	1	CH$_3$	0.9011	0.848	15.03
1	2	CH$_2$	0.6744	0.540	14.03
1	3	CH	0.4469	0.228	13.02
1	4	C	0.2195	0	12.01
2	5	CH$_2$=CH	1.3454	1.176	27.05
2	6	CH=CH	1.1167	0.867	26.04
2	7	CH$_2$=C	1.1173	0.988	26.04
2	8	CH=C	0.8886	0.676	25.03
2	9	C=C	0.6605	0.485	24.02
3	10	ACH	0.5313	0.400	13.02
3	11	AC	0.3652	0.120	12.01
4	12	ACCH$_3$	1.2663	0.968	27.05
4	13	ACCH$_2$	1.0396	0.660	26.04
4	14	ACCH	0.8121	0.348	25.03
5	15	OH	1.0000	1.200	17.01
6	16	CH$_3$OH	1.4311	1.432	32.04
7	17	H$_2$O	0.9200	1.400	18.02
8	18	ACOH	0.8952	0.680	29.02

Sample assignment

	NOGP	IDGP
2,2,-4-Trimethylpentane:		
	5	1
	1	2
	1	3
	1	4
3-Methyl-1-hexene:		
	2	1
	2	2
	1	3
	1	5
Benzene:		
	6	10
Xylene:		
	4	10
	2	12
Ethanol:		
	1	1
	1	2
	1	15
Methanol:		
	1	16
Water:		
	1	17
Phenol:		
	5	10
	1	18

TABLE 8-21 UNIFAC Group Specifications and Sample Group Assignments (Continued)

Group numbers		Name	R	Q	MW	Sample assignment	
Main	Sec.					NOGP	IDGP
9	19	CH$_3$CO	1.6724	1.488	43.05	Methylethylketone:	
9	20	CH$_2$CO	1.4457	1.180	42.04	1	1
						1	2
						1	19
10	21	CHO	0.9980	0.948	29.02	Hexanal:	
						1	1
						4	2
						1	21
11	22	CH$_3$COO	1.9031	1.728	59.04	Butyl acetate:	
11	23	CH$_2$COO	1.6764	1.420	58.04	1	1
						3	2
						1	22
12	24	HCOO	1.2420	1.188	45.02	Ethyl formate:	
						1	1
						1	2
						1	24
13	25	CH$_3$O	1.1450	1.088	31.03	Ethyl ether:	
13	26	CH$_2$O	0.9183	0.780	30.03	2	1
13	27	CH—O	0.6908	0.468	29.02	1	2
13	28	FCH$_2$0	0.9183	1.100	30.03	1	26
14	29	CH$_3$NH$_2$	1.5959	1.544	31.06	Propyl amine:	
14	30	CH$_2$NH$_2$	1.3692	1.236	30.05	1	1
14	31	CHNH$_2$	1.1417	0.924	29.04	1	2
						1	30
15	32	CH$_3$NH	1.4337	1.244	30.05	Diethyl amine:	
15	33	CH$_2$NH	1.2070	0.936	29.04	2	1
15	34	CHNH	0.9795	0.624	28.03	1	2
						1	33

16	35	CH$_3$N	1.1865	0.940	29.04
16	36	CH$_2$N	0.9597	0.632	28.03
17	37	ACNH$_2$	1.0600	0.816	28.03
18	38	C$_5$H$_5$N	2.9993	2.113	79.10
18	39	C$_5$H$_4$N	2.8332	1.833	78.09
18	40	C$_5$H$_3$N	2.6670	1.553	77.09
19	41	CH$_3$CN	1.8701	1.724	41.05
19	42	CH$_2$CN	1.6434	1.416	40.04
20	43	COOH	1.3013	1.224	45.02
20	44	HCOOH	1.5280	1.532	46.03
21	45	CH$_2$Cl	1.4654	1.264	49.48
21	46	CHCl	1.2380	0.952	48.47
21	47	CCl	1.0060	0.724	47.46
22	48	CH$_2$Cl$_2$	2.2564	1.988	84.93
22	49	CHCl$_2$	2.0606	1.684	83.92
22	50	CCl$_2$	1.8016	1.448	82.92
23	51	CHCl$_3$	2.8700	2.410	119.38
23	52	CCl$_3$	2.6401	2.184	118.37
24	53	CCl$_4$	3.3900	2.910	153.82
25	54	ACCl	1.1562	0.844	47.46
26	55	CH$_3$NO$_2$	2.0086	1.868	61.04
26	56	CH$_2$NO$_2$	1.7818	1.560	60.03
26	57	CHNO$_2$	1.5544	1.248	59.02

Triethyl amine:
3 1
2 2
1 36

Aniline:
5 10
1 37

Methyl pyridine:
1 1
1 39

Propionitrile:
1 1
1 42

Acetic acid:
1 1
1 43

Chloroethane:
1 1
1 45

1, 1-Dichloroethane:
1 1
1 49

1, 1, 1-Trichloroethane:
1 1
1 52

Trichloromethane:
1 53

Chlorobenzene:
5 10
1 54

Nitroethane:
1 1
1 56

TABLE 8-21 UNIFAC Group Specifications and Sample Group Assignments (Continued)

| Group numbers | | Name | R | Q | MW | Sample assignment | |
Main	Sec.					NOGP	IDGP
27	58	ACNO$_2$	1.4199	1.104	58.02	Nitrobenzene: 5 / 1	10 / 58
28	59	CS$_2$	2.0570	1.650	76.13	Carbon disulfide: 1	59
29	60	CH$_3$SH	1.8770	1.676	48.10	Ethanethiol: 1	1
29	61	CH$_2$SH	1.6510	1.368	47.09	1	61
30	62	Furfural	3.1680	2.481	96.09	Furfural: 1	62
31	63	(CH$_2$OH)$_2$	2.4088	2.248	62.07	Ethylene glycol: 1	63
32	64	I	1.2640	0.992	126.90	Iodomethane: 1 / 1	1 / 64
33	65	BR	0.9492	0.832	79.90	Bromomethane: 1 / 1	1 / 64
34	66	CH-trip-C	1.2920	1.088	25.03	Propyne: 1 / 1	1 / 66
34	67	C-trip-C	1.0613	0.784	24.02		
35	68	Me$_2$SO	2.8266	2.472	78.13	Dimethylsulfoxide: 1	68
36	69	Acry	2.3144	2.052	53.06	Acrylonitrile: 1	69
37	70	Cl(C=C)	0.7910	0.724	35.45	Trichloroethylene: 1 / 3	8 / 70

No.	Group			
38	ACF	0.6948	0.524	31.01
39	DMF-1	3.0856	2.736	73.09
39	DMF-2	2.6322	2.120	43.03
40	CF$_3$	1.04060	1.380	69.01
40	CF$_2$	1.0105	0.920	50.01
40	CF	0.6150	0.460	31.01
41	COO	1.3800	1.200	44.01
42	SiH$_3$	1.6035	1.263	31.11
42	SiH$_2$	1.4443	1.006	30.10
42	SiH	1.2853	0.749	29.09
42	Si	1.0470	0.410	28.09
43	SiH$_2$O	1.4838	1.062	46.10
43	SiHO	1.3030	0.764	45.09
43	SiO	1.1044	0.466	44.09
44	NMP	3.981	3.20	99.13
45	tert-N	0.2854	0.092	14.01
46	Amide	1.4660	1.336	44.03
47	CON(Me)$_2$	2.8590	2.428	72.09
47	CONMeCH$_2$	2.6320	2.120	71.08
47	CON(CH$_2$)$_2$	2.4050	1.812	70.07

Fluorobenzene:
5 | 10
1 | 71

Dimethylformamide:
1 | 72

Diethylformamide:
2 | 1
1 | 73

Perfluoroethane:
2 | 74

Butylacetate:
2 | 1
3 | 2
1 | 77

Methylsilane:
1 | 1
1 | 78

Hexamethyldisiloxane:
6 | 1
1 | 81
1 | 84

N-Methylpyrrolidone:
1 | 85

Triethylamine:
3 | 1
3 | 2
1 | 86

Acetamide:
1 | 1
1 | 87

N,N-Methylethylamide:
2 | 1
1 | 89

Equation (8-10.55) also holds for $\ln \Gamma_k^{(i)}$. In Eq. (8-10.55), θ_m is the area fraction of group m, and the sums are over all different groups. θ_m is calculated in a manner similar to that for θ_i:

$$\theta_m = \frac{Q_m X_m}{\displaystyle\sum_n Q_n X_n} \tag{8-10.56}$$

where X_m is the mole fraction of group m in the mixture. The group interaction parameter Ψ_{mn} is given by

$$\Psi_{mn} = \exp\left(-\frac{U_{mn} - U_{nn}}{RT}\right) = \exp\left(-\frac{a_{mn}}{T}\right) \tag{8-10.57}$$

where U_{mn} is a measure of the energy of interaction between groups m and n. The group interaction parameters a_{mn} must be evaluated from experimental phase equilibrium data. Note that a_{mn} has units of kelvins and the $a_{mn} \neq a_{nm}$. Parameters a_{mn} and a_{nm} are obtained from a database using a wide range of experimental results. Some of these are shown in Table 8-22. Efforts toward updating and extending Table 8-22 are in progress in several university laboratories.

The combinatorial contribution to the activity coefficient [Eq. (8-10.50)] depends only on the sizes and shapes of the molecules present. As the coordination number z increases, for large-chain molecules $q_i/r_i \rightarrow 1$ and in that limit, Eq. (8-10.50) reduces to the Flory-Huggins equation used in the ASOG method.

The residual contribution to the activity coefficient [Eqs. (8-10.54) and (8-10.55)] depends on group areas and group interaction. When all group areas are equal, Eqs. (8-10.54) and (8-10.55) are similar to those used in the ASOG method.

The functional groups considered in this work are those given in Table 8-21. Whereas each group listed has its own values of R and Q, the subgroups within the same main group, e.g., subgroups 1, 2, and 3 are assumed to have identical energy interaction parameters. We present one example which illustrates (1) the nomenclature and use of Table 8-21 and (2) the UNIFAC method for calculating activity coefficients.

Example 8-11   Obtain activity coefficients for the acetone (1)–n-pentane (2) system at 307 K and $x_1 = 0.047$.

solution   Acetone has one ($\nu_1 = 1$) CH_3 group (main group 1, secondary group 1) and one ($\nu_9 = 1$) CH_3CO group (main group 9, secondary group 19). n-Pentane has two ($\nu_1 = 2$) CH_3 groups (main group 1, secondary group 1) and three ($\nu_1 = 3$) CH_2 groups (main group 1, secondary group 2).
Based on the information in Table 8-21, we can construct the following table:

| Molecule (i) | Group identification | | | $\nu_j^{(i)}$ | R_j | Q_j |
	Name	Main No.	Sec. No.			
Acetone (1)	CH_3	1	1	1	0.9011	0.848
	CH_3CO	9	19	1	1.6724	1.488
n-Pentane (2)	CH_3	1	1	2	0.9011	0.848
	CH_2	1	2	3	0.6744	0.540

We can now write:

$$r_1 = (1)(0.9011) + (1)(1.6724) = 2.5735$$

$$q_1 = (1)(0.848) + (1)(1.488) = 2.336$$

$$\Phi_1 = \frac{(2.5735)(0.047)}{(2.5735)(0.047) + (3.8254)(0.953)} = 0.0321$$

$$\theta_1 = \frac{(2.336)(0.047)}{(2.336)(0.047) + (3.316)(0.953)} = 0.0336$$

$$\ell_1 = (5)(2.5735 - 2.336) - 1.5735 = -0.3860$$

or in tabular form:

Molecule (i)	r_i	q_i	100 Φ_i	100 θ_i	ℓ_i
Acetone (1)	2.5735	2.336	3.21	3.36	-0.3860
n-Pentane (2)	3.8254	3.316	96.79	96.64	-0.2784

We can now calculate the combinatorial contribution to the activity coefficients:

$$\ln \gamma_1^c = \ln \frac{0.0321}{0.047} + (5)(2.336) \ln \frac{0.0336}{0.0321} - 0.3860$$

$$+ \frac{0.0321}{0.047}[(0.047)(0.3860) + (0.953)(0.2784)].$$

$$= -0.0403$$

$$\ln \gamma_2^c = -0.0007$$

Next, we calculate the residual contributions to the activity coefficients. Since only two main groups are represented in this mixture, the calculation is relatively simple. The group interaction parameters a_{mn} are obtained from Table 8-22.

$$a_{1,9} = 476.40$$

$$\Psi_{1,9} = \exp\left(\frac{-476.40}{307}\right)$$

$$= 0.2119$$

$$a_{9,1} = 26.760$$

$$\Psi_{9,1} = \exp\left(\frac{-26.760}{307}\right)$$

$$= 0.9165$$

Note that $\Psi_{1,1} = \Psi_{9,9} = 1.0$, since $a_{1,1} = a_{9,9} = 0$. Let 1 = CH_3, 2 = CH_2, and 19 = CH_3CO.

TABLE 8-22   UNIFAC Group–Group Interaction Parameters, in Kelvins

Main group numbers*	1	2	3	4	5	6	7
1	0	86.020	61.130	76.500	986.500	697.200	1318.000
2	−35.360	0	38.810	74.150	524.100	787.600	270.600
3	−11.120	3.446	0	167.000	636.100	637.300	903.800
4	−69.700	−113.600	−146.800	0	803.200	603.200	5695.000
5	156.400	457.000	89.600	25.820	0	−137.100	353.500
6	16.510	−12.520	−50.000	−44.500	249.100	0	−181.000
7	300.000	496.100	362.300	377.600	−229.100	289.600	0
8	275.800	217.500	25.340	244.200	−451.600	−265.200	−601.800
9	26.760	42.920	140.100	365.800	164.500	108.700	472.500
10	505.700	56.3	23.39	106.0	−404.800	−340.200	232.700
11	114.800	132.100	85.840	−170.000	245.400	249.600	200.8
12	90.490	−62.550	1967	2347.0	191.200	155.700	0
13	83.360	26.510	52.130	65.690	237.700	238.4	−314.700
14	−30.480	1.163	−44.850	0	−164.000	−481.700	−330.400
15	65.330	−28.700	−22.310	223.000	−150.000	−500.400	−448.200
16	−83.980	−25.380	−223.900	109.900	28.600	−406.800	−598.800
17	1139.0	2000.0	247.5	762.8	−17.4	−118.1	−367.8
18	−101.600	0	31.870	49.800	−132.300	−378.200	−332.900
19	24.820	−40.620	−22.970	−138.400	−185.400	157.800	242.800
20	315.300	1264.000	62.320	268.200	−151.000	1020.000	−66.170
21	91.460	97.510	4.680	122.900	562.200	529.000	698.200
22	34.010	18.250	121.300	140.8	747.700	669.900	708.700
23	36.700	51.060	288.500	33.610	742.100	649.100	826.700
24	−78.450	160.900	−4.700	134.700	856.300	860.100	1201.000
25	−141.300	−158.800	−237.700	375.500	246.900	661.600	920.400
26	−32.690	−1.996	10.380	−97.050	261.6	252.600	417.900
27	5541.000	0	1824.000	−127.800	561.600	0	360.700
28	−52.650	16.620	21.500	40.680	823.500	914.200	1081.000
29	−7.481	0	28.410	0	461.600	382.800	0
30	−25.310	0	157.300	404.300	521.600	0	23.480
31	140.000	0	221.400	150.600	267.600	0	−142.1
32	128.000	0	58.680	0	501.300	0	0
33	−31.520	0	155.600	291.100	721.900	494.7	0
34	−72.880	41.380	0	0	0	0	0
35	50.490	422.400	−2.504	−143.200	−25.870	695.000	−240.000
36	−165.900	0	0	0	0	0	386.600
37	47.410	124.200	395.800	0	738.900	528.000	0
38	−5.132	0	−237.200	−157.300	649.700	645.900	0
39	−31.950	249.000	−133.900	−240.200	64.160	172.200	−287.100
40	147.300	0	0	0	0	0	0
41	529.000	1397.000	317.600	615.800	88.630	171.000	284.400
42	−34.36	0	787.9	191.600	1913.0	0	0
43	110.2	0	234.4	221.800	84.850	0	0
44	13.89	0	−23.88	6.214	796.9	0	832.2
45	272.000	0	−288.000	−1020.000	0	−668.000	−1080.000
46	8960.000	−963.000	−63.100	−196.000	0	0	0
47	−11.100	0	−11.800	−36.600	0	0	0

Main group numbers	8	9	10	11	12	13	14
1	1333.000	476.400	677.000	232.100	741.400	251.500	391.500
2	526.100	182.600	448.8	37.850	449.100	214.500	240.900
3	1329.000	25.770	347.3	5.994	−92.55	32.140	161.700
4	884.900	−52.100	586.6	5688.000	115.2	213.100	0
5	−259.700	84.000	441.800	101.100	193.100	28.060	83.020
6	−101.700	23.390	306.400	−10.720	193.400	−128.6	359.300
7	324.500	−195.400	−257.300	72.87	0	540.500	48.890
8	0	−356.100	0	−449.400	0	0	0
9	−133.100	0	−37.360	−213.700	−38.47	−103.6	0
10	0	128.000	0	−110.3	11.31	304.100	0
11	−36.720	372.200	185.1	0	372.900	−235.700	0
12	0	70.42	35.35	−261.100	0	0	0
13	0	191.1	−7.838	461.300	0	0	0
14	0	0	0	0	0	0	0
15	0	0	0	136.000	0	−49.300	108.800
16	0	225.3	0	0	0	0	38.890
17	−253.1	−450.3	0	−294.8	0	0	−15.07
18	−341.600	−51.540	0	0	0	0	0
19	0	−287.500	0	−266.600	0	38.81	0
20	0	−297.800	0	−256.300	312.500	−338.500	0
21	0	286.300	−47.510	35.38	0	225.400	0
22	0	423.200	0	−132.900	0	−197.700	0
23	0	552.100	242.8	176.500	488.900	−20.930	0
24	10000.000	372.000	0	129.500	403.1	113.900	261.100
25	0	128.100	0	−246.300	0	95.5	203.500
26	0	−142.600	0	129.3	0	−94.490	0
27	0	0	0	0	0	0	0
28	0	303.700	0	243.800	0	112.400	0
29	0	160.600	0	0	239.800	63.710	106.700
30	0	317.500	0	−146.300	0	0	0
31	838.400	0	0	152.000	0	9.207	0
32	0	138.000	0	21.920	0	476.600	0
33	0	−142.600	0	24.37	0	736.400	0
34	0	443.600	0	0	0	0	0
35	0	110.400	0	41.570	0	−122.100	0
36	0	0	0	175.5	0	0	0
37	0	−40.900	0	16.990	0	−217.900	0
38	0	0	0	0	0	167.1	0
39	0	97.040	0	0	0	−158.200	0
40	0	0	0	0	0	0	0
41	−167.300	123.400	0	−234.900	65.370	−247.800	0
42	0	992.4	0	0	0	0	0
43	0	0	0	0	0	0	0
44	0	0	0	0	0	0	0
45	0	−435.000	−686.000	−463.000	0	2880.000	0
46	0	−444.000	−167.000	0	0	−74.700	0
47	0	1530.000	−60.800	−466.000	0	0	0

TABLE 8-22   UNIFAC Group–Group Interaction Parameters, in Kelvins   (Continued)

Main group numbers*	15	← 16	17	18	19	20	21
1	225.700	206.600	920.7	287.700	597.000	663.500	35.930
2	163.900	61.110	749.3	0	336.900	318.900	204.600
3	122.800	90.490	648.2	−4.449	212.500	537.400	−18.810
4	−49.290	23.500	664.2	52.800	6096.000	603.800	−114.100
5	42.700	−323.000	−52.39	170.000	6.712	199.000	75.620
6	266.000	53.900	489.7	580.500	36.230	−289.500	−38.320
7	168.000	304.000	−52.29	459.000	112.600	−14.090	325.400
8	0	0	119.9	−305.500	0	0	0
9	0	−169.0	6201.0	165.100	481.700	669.400	−191.700
10	0	0	0	0	0	0	751.900
11	−73.500	0	475.5	0	494.600	660.200	−34.74
12	0	0	0	0	0	−356.300	0
13	141.700	0	0	0	−18.51	664.600	301.100
14	63.720	−41.110	−200.7	0	0	0	0
15	0	−189.200	0	0	0	0	0
16	865.900	0	0	0	0	0	0
17	0	0	0	0	−281.6	0	287.0
18	0	0	0	0	−169.700	−153.700	0
19	0	0	777.4	134.300	0	0	88.75
20	0	0	0	−313.500	0	0	44.420
21	0	0	429.7	0	−62.41	326.4	0
22	0	−141.400	0	587.300	258.6	339.6	−84.530
23	0	−293.700	0	18.980	74.040	1346.000	−157.100
24	91.130	−126.000	898.2	309.200	492.000	689.000	11.800
25	−108.400	1088.000	530.5	0	356.900	0	−314.900
26	0	0	0	0	0.2830	0	113.0
27	0	0	134.9	0	0	0	0
28	0	0	0	0	335.700	0	−73.090
29	0	0	0	0	125.700	0	−27.940
30	0	0	0	0	0	0	0
31	0	0	255.4	0	0	0	0
32	0	0	0	0	0	0	0
33	0	0	0	0	0	5256.0	1169.000
34	0	0	0	0	329.100	0	0
35	0	−257.2	0	0	0	150.0	0
36	0	0	0	0	−42.310	0	0
37	0	0	0	0	304.000	898.200	428.500
38	0	116.5	0	0	0	0	0
39	0	0	343.7	0	0	−106.6	0
40	0	0	0	0	0	0	0
41	284.500	0	−22.1	0	−61.600	1179.000	182.2
42	0	0	0	0	0	2450.000	0
43	0	0	0	0	0	2496.000	0
44	0	0	0	0	0	0	0
45	0	0	0	0	0	0	0
46	0	0	0	0	0	0	0
47	0	0	0	0	0	0	0

Main group numbers	22	23	24	25	26	27	28
1	53.760	24.900	104.300	321.500	661.500	543.000	153.600
2	5.892	−13.990	−109.700	393.100	357.500	0	76.300
3	−144.400	−231.900	3.000	538.200	168.000	194.900	52.070
4	−111.0	−12.140	−141.300	−126.900	3629.000	4448.000	−9.451
5	−112.100	−98.120	143.100	287.800	256.5	157.100	477.000
6	−102.500	−139.400	−67.800	17.120	75.140	0	−31.090
7	370.400	353.700	497.500	678.200	220.600	399.500	887.100
8	0	0	1827.000	0	0	0	0
9	−284.000	−354.600	−39.200	174.500	137.500	0	216.100
10	0	−483.7	0	0	0	0	0
11	108.900	−209.700	54.470	629.000	−81.13	0	183.000
12	0	−287.200	36.84	0	0	0	0
13	137.800	−154.300	47.670	66.15	95.180	0	140.900
14	0	0	−99.810	68.810	0	0	0
15	0	0	71.230	4350.000	0	0	0
16	−73.850	−352.900	−8.283	−86.360	0	0	0
17	0	0	882.0	287.9	0	−139.3	0
18	−351.600	−114.700	−165.100	0	0	0	0
19	−152.7	−15.620	−54.860	52.310	−0.515	0	230.900
20	120.2	76.750	212.700	0	0	0	0
21	108.300	249.200	62.420	464.400	32.73	0	450.100
22	0	0	56.330	0	0	0	0
23	0	0	−30.100	0	0	0	116.600
24	17.970	51.900	0	475.800	490.900	534.700	132.200
25	0	0	−255.400	0	−154.5	0	0
26	0	0	−34.680	794.400	0	533.200	0
27	0	0	514.600	0	−85.120	0	0
28	0	−26.060	−60.710	0	0	0	0
29	0	0	0	0	0	0	0
30	0	48.480	−133.100	0	0	0	0
31	0	0	0	0	481.300	0	0
32	−40.820	21.760	48.490	0	64.280	0	0
33	0	0	225.800	224.000	125.300	0	0
34	0	0	0	0	174.400	0	0
35	−215.000	−343.600	−58.430	0	0	0	0
36	0	0	−85.15	0	0	0	0
37	0	−149.800	−134.200	0	379.400	0	167.900
38	0	0	−124.600	0	0	0	0
39	0	0	−186.700	0	0	0	0
40	0	0	0	0	0	0	0
41	305.400	−193.000	335.700	1107.000	−124.7	0	885.500
42	0	0	0	0	0	0	0
43	0	0	70.81	0	0	0	0
44	0	0	0	0	0	0	0
45	0	0	0	0	0	0	0
46	0	0	0	0	0	0	0
47	0	0	0	0	0	0	0

TABLE 8-22   UNIFAC Group–Group Interaction Parameters, in Kelvins   (*Continued*)

Main group numbers	29	30	31	32	33	34	35
1	184.400	354.500	3025.000	335.800	479.500	298.900	526.500
2	0	0	0	0	0	31.140	−137.400
3	−10.430	−64.690	210.400	113.300	−13.590	0	169.900
4	0	−20.360	4975.000	0	−171.300	0	4284.000
5	147.500	−120.500	−318.900	313.500	133.400	0	−202.100
6	37.840	0	0	0	106.3	0	−399.300
7	0	188.000	13.53	0	0	0	−139.000
8	0	0	−687.100	0	0	0	0
9	−46.280	−163.700	0	53.590	245.200	−246.600	−44.580
10	0	0	0	0	0	0	0
11	0	202.300	−101.700	148.300	18.88	0	52.080
12	4.339	0	0	0	0	0	0
13	−8.538	0	−20.110	−149.500	−202.300	0	172.100
14	−70.140	0	0	0	0	0	0
15	0	0	0	0	0	0	0
16	0	0	0	0	0	0	243.1
17	0	0	−136.9	0	0	0	0
18	0	0	0	0	0	0	0
19	21.370	0	0	0	0	−203.000	0
20	0	0	0	0	−95.0	0	−561.2
21	59.020	0	0	0	−125.9	0	0
22	0	0	0	177.600	0	0	215.000
23	0	−64.380	0	86.400	0	0	363.700
24	0	546.700	0	247.800	41.940	0	337.700
25	0	0	0	0	−60.700	0	0
26	0	0	139.800	304.300	10.170	−27.700	0
27	0	0	0	0	0	0	0
28	0	0	0	0	0	0	0
29	0	0	0	0	0	0	31.660
30	0	0	0	0	0	0	0
31	0	0	0	0	0	0	−417.200
32	0	0	0	0	0	0	0
33	0	0	0	0	0	0	0
34	0	0	0	0	0	0	0
35	85.700	0	535.800	0	0	0	0
36	0	0	0	0	0	0	0
37	0	0	0	0	0	0	0
38	0	0	0	0	0	0	0
39	−71.000	0	−191.700	0	0	6.699	136.600
40	0	0	0	0	0	0	0
41	0	0	0	288.100	0	0	−29.340
42	0	0	0	0	0	0	0
43	0	0	0	0	0	0	0
44	0	0	0	0	0	0	0
45	0	0	0	0	0	0	0
46	0	0	0	0	0	0	0
47	0	0	0	0	0	0	0

Main group numbers	36	37	38	39	40	41	42
1	689.000	−4.189	125.800	485.300	−2.859	387.100	−450.4
2	0	−66.460	0	−70.450	0	48.330	0
3	0	−259.100	389.300	245.600	0	103.500	−432.3
4	0	0	101.400	5629.000	0	69.260	683.300
5	0	225.800	44.780	−143.900	0	190.300	−817.7
6	0	33.470	−48.250	−172.400	0	165.700	0
7	160.800	0	0	319.000	0	−197.500	0
8	0	0	0	0	0	−494.200	
9	0	−34.570	0	−61.700	0	−18.800	0
10	0	0	0	0	0	0	0
11	−28.61	−83.300	0	0	0	560.200	0
12	0	0	0	0	0	−70.240	0
13	0	240.200	−273.9	254.800	0	417.000	0
14	0	0	0	0	0	0	0
15	0	0	0	0	0	−38.770	0
16	0	0	−196.3	0	0	0	0
17	0	0	0	−334.4	0	−89.42	0
18	0	0	0	0	0	0	0
19	81.570	3.509	0	0	0	120.300	0
20	0	−11.160	0	−246.5	0	−337.000	169.300
21	0	−245.400	0	0	0	63.67	0
22	0	0	0	0	0	−96.870	0
23	0	111.200	0	0	0	255.800	0
24	369.5	187.100	215.200	498.600	0	256.500	639.300
25	0	0	0	0	0	−145.100	0
26	0	10.760	0	0	0	248.4	0
27	0	0	0	0	0	0	0
28	0	−47.370	0	0	0	469.800	0
29	0	0	0	78.920	0	0	0
30	0	0	0	0	0	0	0
31	0	0	0	302.200	0	0	0
32	0	0	0	0	0	68.550	0
33	0	0	0	0	0	0	0
34	0	0	0	−119.800	0	0	0
35	0	0	0	−97.710	0	153.700	0
36	0	0	0	0	0	423.400	0
37	0	0	0	0	0	730.800	0
38	0	0	0	0	−117.2	0	0
39	0	0	0	0	0	0	0
40	0	0	185.6	0	0	0	0
41	−53.910	−198.000	0	0	0	0	0
42	0	0	0	0	0	0	0
43	0	0	0	0	0	0	745.3
44	0	0	0	0	0	0	0
45	0	0	0	0	0	0	0
46	0	0	0	0	0	0	0
47	0	0	0	0	0	0	0

TABLE 8-22   UNIFAC Group–Group Interaction Parameters, in Kelvins   (*Continued*)

Main group numbers*	43	44	45	46	47
1	252.7	220.3	383.000	−1380.000	729.000
2	0	0	0	2340.000	0
3	238.9	30.04	109.000	75.900	784.000
4	355.500	46.38	1320.000	482.000	386.000
5	202.700	−504.2	0	0	0
6	0	0	214.000	0	0
7	0	−452.2	365.000	0	0
8	0	0	0	0	0
9	0	0	135.000	−1680.000	−58.000
10	0	0	−7.180	333.000	6810.000
11	0	0	−54.600	0	6960.000
12	0	0	0	0	0
13	0	0	5780.000	131.000	0
14	0	0	0	0	0
15	0	0	0	0	0
16	0	0	0	0	0
17	0	0	0	0	0
18	0	0	0	0	0
19	0	0	0	0	0
20	127.200	0	0	0	0
21	0	0	0	0	0
22	0	0	0	0	0
23	0	0	0	0	0
24	0	0	0	0	0
25	0	0	0	0	0
26	0	0	0	0	0
27	0	0	0	0	0
28	0	0	0	0	0
29	0	0	0	0	0
30	0	0	0	0	0
31	0	0	0	0	0
32	0	0	0	0	0
33	0	0	0	0	0
34	0	0	0	0	0
35	0	0	0	0	0
36	0	0	0	0	0
37	0	0	0	0	0
38	0	0	0	0	0
39	0	0	0	0	0
40	0	0	0	0	0
41	0	0	0	0	0
42	−2166.0	0	0	0	0
43	0	0	0	0	0
44	0	0	0	0	0
45	0	0	0	0	0
46	0	0	0	0	0
47	0	0	0	0	0

*Parameters for groups 45 to 47 were estimated from gas-liquid chromatographic data. While the accuracy of these parameters is not as high as that obtained from reduction of conventional vapor-liquid equilibrium data, these parameters appreciably extend the range of applicability of UNIFAC.

Next we compute $\Gamma_k^{(i)}$, the residual activity coefficient of group k in a reference solution containing only molecules of type i. For pure acetone (1), the mole fraction of group m, X_m, is

$$X_1^{(1)} = \frac{\nu_1^{(1)}}{\nu_1^{(1)} + \nu_{19}^{(1)}} = \frac{1}{1+1} = \frac{1}{2} \qquad X_{19}^{(1)} = \frac{1}{2}$$

Hence

$$\theta_1^{(1)} = \frac{\frac{1}{2}(0.848)}{\frac{1}{2}(0.848) + \frac{1}{2}(1.488)}$$

$$= 0.363 \qquad \theta_{19}^{(1)} = 0.637$$

$$\ln \Gamma_1^{(1)} = 0.848 \left\{ 1 - \ln[0.363 + (0.637)(0.9165)] \right.$$

$$\left. - \left[\frac{(0.363)}{0.363 + 0.637(0.9165)} + \frac{(0.637)(0.2119)}{(0.363)(0.2119) + 0.637} \right] \right\}$$

$$= 0.409$$

$$\ln \Gamma_{19}^{(1)} = 1.488 \left\{ 1 - \ln[(0.363)(0.2119) + 0.637] \right.$$

$$\left. - \left[\frac{(0.363)(0.9165)}{0.363 + (0.637)(0.9165)} + \frac{0.637}{(0.363)(0.2119) + 0.637} \right] \right\}$$

$$= 0.139$$

For pure n-pentane (2), the mole fraction of group m, X_m, is

$$X_1^{(2)} = \frac{\nu_1^{(2)}}{\nu_1^{(2)} + \nu_2^{(2)}} = \frac{2}{2+3} = \frac{2}{5} \qquad X_2^{(2)} = \frac{3}{5}$$

Since only one main group is in n-pentane (2),

$$\ln \Gamma_1^{(2)} = \ln \Gamma_2^{(2)} = 0.0$$

The group residual activity coefficients can now be calculated for $x_1 = 0.047$:

$$X_1 = \frac{(0.047)(1) + 0.953(2)}{(0.047)(2) + 0.953(5)} = 0.4019 \qquad X_2 = 0.5884 \qquad X_{19} = 0.0097$$

$$\theta_1 = \frac{(0.848)(0.4019)}{(0.848)(0.4019) + (0.540)(0.5884) + (1.488)(0.0097)} = 0.5064$$

$$\theta_2 = 0.4721 \qquad \theta_{19} = 0.0214$$

$$\ln \Gamma_1 = 0.848 \left\{ 1 - \ln[0.5064 + 0.4721 + (0.0214)(0.9165)] \right.$$

$$\left. - \left[\frac{0.5064 + 0.4721}{0.5064 + 0.4721 + (0.0214)(0.9165)} + \frac{(0.0214)(0.2119)}{(0.5064 + 0.4721)(0.2119) + 0.0214} \right] \right\}$$

$$= 1.45 \times 10^{-3}$$

$$\ln \Gamma_2 = 0.540 \left\{ 1 - \ln[0.5064 + 0.4721 + (0.0214)(0.9165)] \right.$$

$$\left. - \left[\frac{0.5064 + 0.4721}{0.5064 + 0.4721 + (0.0214)(0.9165)} + \frac{(0.0214)(0.2119)}{(0.5064 + 0.4721)(0.2119) + 0.0214} \right] \right\}$$

$$= 9.26 \times 10^{-4}$$

$$\ln \Gamma_{19} = 1.488 \left\{ 1 - \ln[(0.5064 + 0.4721)(0.2119) + 0.214] \right.$$

$$\left. - \left[\frac{(0.5064 + 0.4721)(0.9165)}{0.5064 + 0.4721 + (0.0214)(0.9165)} + \frac{0.0214}{(0.5064 + 0.4721)(0.2119) + 0.0214} \right] \right\}$$

$$= 2.21$$

The residual contributions to the activity coefficients follow

$$\ln \gamma_1^R = (1)(1.45 \times 10^{-3} - 0.409) + (1)(2.21 - 0.139) = 1.66$$

$$\ln \gamma_2^R = (2)(1.45 \times 10^{-3} - 0.0) + 3(9.26 \times 10^{-4} - 0.0) = 5.68 \times 10^{-3}$$

Finally, we calculate the activity coefficients:

$$\ln \gamma_1 = \ln \gamma_1^C + \ln \gamma_1^R = -0.0403 + 1.66 = 1.62$$

$$\ln \gamma_2 = \ln \gamma_2^C + \ln \gamma_2^R = -0.0007 + 5.68 \times 10^{-3} = 4.98 \times 10^{-3}$$

Hence,

$$\gamma_1 = 5.07 \qquad \gamma_2 = 1.01$$

The corresponding experimental values of Lo et al. [70] are:

$$\gamma_1 = 4.41 \qquad \gamma_2 = 1.11$$

Although agreement with experiment is not as good as we might wish, it is not bad and it is representative of what UNIFAC can do. The main advantage of UNIFAC is its wide range of application.†

8-11   Solubilities of Gases in Liquids

At modest pressures, most gases are only sparingly soluble in typical liquids. For example, at 25°C and a partial pressure of 1.01 bar, the (mole fraction) solubility of nitrogen in cyclohexane is $x = 7.6 \times 10^{-4}$ and that in water is $x = 0.18 \times 10^{-4}$. Although there are some exceptions (notably, hydrogen), the solubility of a gas in typical solvents usually falls with rising temperature. However, at higher temperatures, approaching the critical temperature of the solvent, the solubility of a gas usually rises with temperature, as illustrated in Fig. 8-13.

Experimentally determined solubilities have been reported in the chemical literature for over 100 years, but many of the data are of poor quality. Although no truly comprehensive and critical compilation of the available data exists, Table 8-23 gives some useful data sources.

Unfortunately, a variety of units has been employed in reporting gas solubilities. The most common of these are two dimensionless coefficients: *Bunsen coefficient*, defined as the volume (corrected to 0°C and 1 atm) of gas dissolved per unit volume of solvent at system temperature T when the partial pressure of the solute is 1 atm; *Ostwald coefficient*, defined as

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†Tables 8-21 and 8-22 are periodically revised and extended. The version shown here is based on results reported by Tiegs et al. [119a] and previous authors referenced by Tiegs. For the latest versions, contact J. M. Prausnitz, Department of Chemical Engineering, University of California, Berkeley.

TABLE 8-23 Some Sources for Solubilities of Gases in Liquids

Washburn, E. W., (ed.): *International Critical Tables*, McGraw-Hill, New York, 1926.

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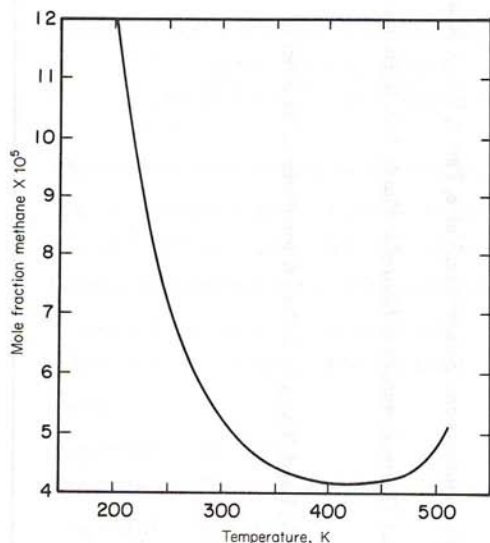
Figure 8-13 Solubility of methane in n-heptane when vapor phase fugacity of methane is 0.0101 bar. *(From Ref. 97.)*

the volume of gas at system temperature T and partial pressure p dissolved per unit volume of solvent. If the solubility is small and the gas phase is ideal, the Ostwald coefficient is independent of p and these two coefficients are simply related by

$$\text{Ostwald coefficient} = \frac{T}{273} \text{ (Bunsen coefficient)}$$

where T is in kelvins. Adler [5], Battino [11], and Friend and Adler [37] have discussed these and other coefficients for expressing solubilities as well as some of their applications for engineering calculations.

These units are often found in older articles. In recent years it has become more common to report solubilities in units of mole fraction or Henry's constants.

When the solubility is small, Henry's law provides a good approximation. In a binary system let subscript 2 refer to the gaseous solute and subscript 1 to the liquid solvent. Henry's law is written

$$f_2 = H_{2,1}^{(P_{vp1})} x_2 \qquad x_2 \ll 1 \tag{8-11.1}$$

where x is the mole fraction, f is the fugacity, and H is Henry's constant, rigorously defined by

$$H_{2,1}^{(P_{vp1})} = \lim_{x_2 \to 0} \left(\frac{f}{x}\right)_2 \tag{8-11.2}$$

The subscript 2,1 indicates that Henry's constant H is for solute 2 in solvent 1. Superscript P_{vp1} indicates that the pressure of the system (as $x_2 \to$

0) is equal to the saturation (vapor) pressure of solvent 1 at temperature T. Henry's constant depends on temperature, and often strongly so.

If the gas pressure is large, the effect of pressure on Henry's constant must be taken into consideration. In that event, Eq. (8-11.1) takes the more general form

$$\ln\left(\frac{f}{x}\right)_2 = \ln\left(\frac{\phi y P}{x}\right)_2 = \ln H_{2,1}^{(P_{vp1})} + \frac{\overline{V}_2^{\infty}(P - P_{vp1})}{RT} \qquad (8\text{-}11.3)$$

where ϕ = vapor phase fugacity coefficient
  P = system pressure
  $\overline{V}_2^{\infty}$ = partial molar volume of solute 2 at infinite dilution in the liquid
     phase
  R = gas constant

[Equation (8-11.3) assumes that $\overline{V}_2^{\infty}$ is independent of pressure in the interval $P - P_{vp1}$.] An illustration of how it can be used to reduce solubility data is given in Fig. 8-14 which shows the solubility of nitrogen in water. In this case, since the vapor phase is predominantly nitrogen, the fugacity coefficient for nitrogen is calculated by using the Lewis fugacity rule.† The important assumption in Eq. (8-11.3) is that x_2 is small com-

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†The Lewis fugacity rule assumes that $\phi_i^V(T, P, y_i) = \phi_i^V(T, P, y_i = 1)$, where superscript V refers to the vapor phase.
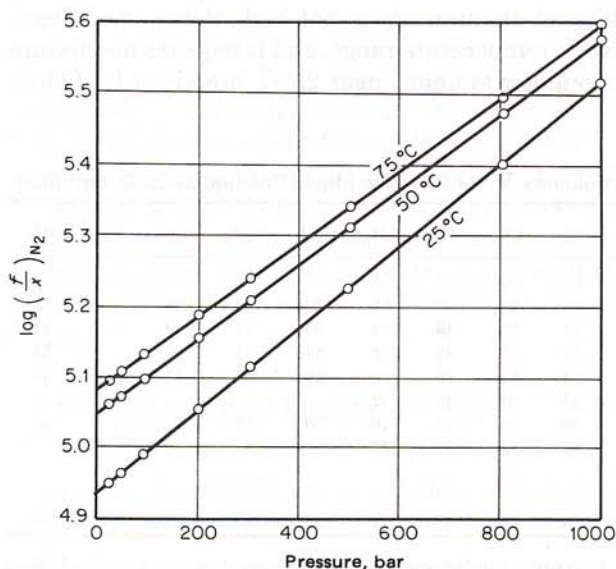
Figure 8-14 Solubility of nitrogen in water at high pressures. *(From Ref. 97.)*

pared with unity. Just what "small" means depends on the chemical nature of the solute and solvent, as discussed elsewhere [97]. In general, the larger the difference in chemical nature between solute and solvent, the smaller x_2 must be for Eq. (8-11.3) to hold.

In Eq. (8-11.3), the first term on the right-hand side is always dominant; the second term is a correction. Correlations for $\overline{V}_2^\infty$ have been presented by Lyckman et al. [71], by Brelvi and O'Connell [20], and by Tiepel and Gubbins [120]. Some typical values for $\overline{V}_2^\infty$ quoted by Hildebrand and Scott are shown in Table 8-24. At temperatures well below the solvent's critical temperature, $\overline{V}^\infty$ is larger than, but in the vicinity of, the solute's molar volume at its normal boiling temperature. However, $\overline{V}^\infty$ may become much larger at temperatures close to the critical temperature of the solvent [97].

Many attempts have been made to correlate gas solubilities, but success has been severely limited because, on the one hand, a satisfactory theory for gas-liquid solutions has not been established and, on the other, reliable experimental data are not plentiful, especially at temperatures remote from 25°C. Among others, Battino and Wilhelm [12] have obtained some success in correlating solubilities in nonpolar systems near 25°C by using concepts from perturbed-hard-sphere theory, but, as yet, these are of limited use for engineering work. A more useful graphical correlation, including polar systems, was prepared by Hayduk et al. [49], and a correlation based on regular solution theory for nonpolar systems was established by Prausnitz and Shair [100] and, in similar form, by Yen and McKetta [136]. The regular solution correlation is limited to nonpolar (or weakly polar) systems, and although its accuracy is not high, it has two advantages: it applies over a wide temperature range, and it requires no mixture data. Correlations for nonpolar systems, near 25°C, are given by Hildebrand and Scott [54].

TABLE 8-24   Partial Molal Volumes $\overline{V}^\infty$ of Gases in Liquid Solution at 25°C, cm³/mol†

	H₂	N₂	CO	O₂	CH₄	C₂H₂	C₂H₄	C₂H₆	CO₂	SO₂
Ethyl ether	50	66	62	56	58					
Acetone	38	55	53	48	55	49	58	64	...	68
Methyl acetate	38	54	53	48	53	49	62	69	...	47
Carbon tetrachloride	38	53	53	45	52	54	61	67	...	54
Benzene	36	53	52	46	52	51	61	67	...	48
Methanol	35	52	51	45	52	...	...	...	43	
Chlorobenzene	34	50	46	43	49	50	58	64	...	48
Water	26	40	36	31	37	...	...	...	33	
Molar volume of pure solute at its normal boiling point	28	35	35	28	39	42	50	55	40	45

†J. H. Hildebrand and R. L. Scott, "Solubility of Nonelectrolytes," 3d ed., Reinhold, New York, 1950.

A crude estimate of solubility can be obtained rapidly by extrapolating the vapor pressure of the gaseous solute on a linear plot of log P_{vp} vs. $1/T$. The so-called *ideal solubility* is given by

$$x_2 = \frac{y_2 P}{P_{vp2}} \tag{8-11.4}$$

where P_{vp2} is the (extrapolated) vapor pressure of the solute at system temperature T. The ideal solubility is a function of temperature, but it is independent of the solvent. Table 8-25 shows that for many typical cases, Eq. (8-11.4) provides an order-of-magnitude estimate.

TABLE 8-25   Solubilities of Gases in Several Liquid Solvents at 25°C and 1.01 bar Partial Pressure. Mole Fraction $\times$ 10⁴

	Ideal†	n-C_7F_{16}	n-C_7H_{16}	CCl_4	CS_2	$(CH_3)_2CO$
H_2	8	14.01	6.88	3.19	1.49	2.31
N_2	10	38.7	...	6.29	2.22	5.92
CH_4	35	82.6	...	28.4	13.12	22.3
CO_2	160	208.8	121	107	32.8	

†See Eq. (8-11.4).

To find the solubility of a gas in a mixed solvent, a first approximation is provided by the expression

$$\ln H_{2,mix} = \sum_{\substack{i=1,3,\ldots \\ i \neq 2}} x_i \ln H_{2,i} \tag{8-11.5}$$

where $H_{2,mix}$ is Henry's constant for solute 2 in the solvent mixture and $H_{2,i}$ is Henry's constant for solute 2 in solvent i, both at system temperature. The mole fraction x_i is on a solute-free basis.

Equation (8-11.5) is rigorous when the solvent mixture is ideal. However, even for nonideal mixtures, this equation provides a reasonable approximation. For more accurate estimates, it is necessary to add to Eq. (8-11.5) terms which depend on the nonideality of the solvent mixture [86, 120].

8-12   Vapor-Liquid Equilibria at High Pressures

Vapor-liquid equilibrium calculations at high pressures are more difficult than those at low or modest pressures for several reasons.

1. The effect of pressure on liquid phase properties is significant only at high pressures. At low or modest pressures this effect can often be

neglected or approximated; the common approximation is to assume in Eq. (8-2.3) that the standard-state fugacity depends on pressure (as given by the Poynting factor) but the activity coefficient is independent of pressure at constant composition and temperature. Since

$$\left(\frac{\partial \ln \gamma_i}{\partial P}\right)_{T,x} = \frac{\overline{V}_i^L - V_{\text{pure }i}^L}{RT} \tag{8-12.1}$$

the assumption that activity coefficient γ_i is independent of pressure is equivalent to assuming that in the liquid phase the partial molar volume $\overline{V}_i^L$ is equal to the molar volume of pure liquid i. At high pressures, especially in the critical region, this assumption can lead to serious error.

2. The vapor phase fugacity coefficient ϕ_i must be found from an equation of state suitable for high pressures, as discussed in Sec. 5-8. Such equations tend to be complex. By contrast, at low pressures we can often set $\phi_i = 1$, and at modest pressures we can often calculate ϕ_i with the virial equation truncated after the second term.

3. In high-pressure vapor-liquid equilibria we frequently must deal with supercritical components; we are often concerned with mixtures at a temperature which is larger than the critical temperature of one (or possibly more) of the components. In that event, how do we evaluate the standard-state fugacity of the supercritical component? Normally we use as a standard state the pure liquid at system temperature and pressure. For a supercritical component the pure liquid at system temperature is hypothetical, and therefore there is no unambiguous way to calculate its fugacity. The problem of supercritical hypothetical standard states can be avoided by using the unsymmetric convention for normalizing activity coefficients [97, chap. 6], and some correlations for engineering use have been established on that basis [86, 98]. However, there are computational disadvantages in using unsymmetrically normalized activity coefficients, especially in multicomponent systems, and therefore their use in engineering work is not popular.

4. In high-pressure vapor-liquid equilibria we frequently encounter critical phenomena, including retrograde condensation. Since these phenomena are not well understood, it is difficult to establish simple algebraic equations for representing them.

Vapor-liquid equilibria at high pressures are conveniently calculated by using an equation of state applicable to both phases.

High-pressure vapor-liquid equilibria are often expressed in terms of K factors: For any component i.

$$K_i = \frac{y_i}{x_i} \tag{8-12.2}$$

where y is the mole fraction in the vapor phase and x is the mole fraction in the liquid phase. Equation (8-12.2) can be rewritten in terms of fugacity coefficients which can be calculated from an equation of state.

The condition for phase equilibrium is

$$f_i^V = f_i^L \tag{8-12.3}$$

where f is fugacity and superscripts V and L denote vapor phase and liquid phase, respectively. Since, for each phase, fugacity coefficient ϕ_i' is defined by

$$\phi_i^V = \frac{f_i^V}{y_i P} \tag{8-12.4a}$$

and

$$\phi_i^L = \frac{f_i^L}{x_i P} \tag{8-12.4b}$$

it follows that

$$K_i = \frac{y_i}{x_i} = \frac{\phi_i^L}{\phi_i^V} \tag{8-12.5}$$

Assuming that we have available an equation of state of the form

$$P = F(T, V, z_1, z_2, \ldots) \tag{8-12.6}$$

and assuming further that this equation of state holds for all fluid densities (i.e., gases and liquids) and for all compositions $z_1 z_2, \ldots$, we can then calculate ϕ_i^L and ϕ_i^V from

$$RT \ln \phi_i^L = \int_{VL}^{\infty} \left[\left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_j} - \frac{RT}{V} \right] dV - RT \ln Z^L \tag{8-12.7a}$$

$$RT \ln \phi_i^V = \int_{VV}^{\infty} \left[\left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_j} - \frac{RT}{V} \right] dV - RT \ln Z^V \tag{8-12.7b}$$

where compressibility factor Z is given by

$$Z^L = \frac{PV^L}{RT} \tag{8-12.8a}$$

$$Z^V = \frac{PV^V}{RT} \tag{8-12.8b}$$

In the liquid phase, the total volume V_T^L is related to the molar volume V^L by

$$V^L = \frac{V_T^L}{n_T^L} \tag{18-12.9a}$$

where n_T^L is the total number of moles in the liquid phase. Similarly,

$$V^V = \frac{V_T^V}{n_T^V} \tag{8-12.9b}$$

In principle. Eqs. (8-12.5) to (8-12.8) are sufficient to find all K factors in a multicomponent system containing two (or more) fluid phases. However, if a realistic equation of state is used, the required computations are strongly nonlinear and often require extensive iterations.

To fix ideas, consider a two-phase (vapor-liquid) system containing m components at a fixed total pressure P. The mole fractions in the liquid phase are $x_1, x_2, \ldots, x_{m-1}$. We want to find the bubble point temperature T and the vapor phase mole fractions $y_1, y_2, \ldots, y_{m-1}$. The total number of unknowns, therefore, is m. However, to use Eqs. (8-12.7a) and (8-12.7b), we also must know the molar volumes V^L and V^V. Therefore, the total number of unknowns is $m + 2$.

To find $m + 2$ unknowns, we require $m + 2$ independent equations. These are:

Equation (8-12.5) for each component i: m equations

Equation (8-12.6), once for the vapor phase

and once for the liquid phase: 2 equations

Total number of independent equations: $m + 2$

This case, in which P and x are given and T and y are to be found, is called a bubble point T problem. Other common cases are:

Given variables	Variables to be found	Name
P, y	T, x	Dew point T
T, x	P, y	Bubble point P
T, y	P, x	Dew point P

However, the most common problem in process design is the flash problem in which we are given P, T, and the total (feed) composition; we must then find x, y, and α, where α is the fraction of feed which is vaporized in the flash chamber. We cannot go into details here; numerous articles have discussed computational procedures for solving flash problems with an equation of state [50, 78]. A useful discussion is given by Topliss (122).

Knapp et al. [61] have presented a comprehensive (877-page) monograph on calculation of vapor-liquid equilibria by using an equation of state. The monograph contains an exhaustive literature survey (1900–

1980) of experimental data for binary mixtures encountered in natural gas and petroleum technology: hydrocarbons, common gases, freons, and a few oxygenated hydrocarbons. Knapp considered four equations of state:

1. LKP. An equation of state of the Benedict-Webb-Rubin form, proposed by Lee and Kesler [67], based on Pitzer's extended theory of corresponding states where compressibility factor Z of a fluid consists of two parts:

$$Z(P, T) = Z^{(0)} \left(\frac{P}{P_c}, \frac{T}{T_c} \right) + \omega Z^{(1)} \left(\frac{P}{P_c}, \frac{T}{T_c} \right) \tag{8-12.10}$$

Here P_c and T_c are the critical pressure and temperature and ω is the acentric factor, $Z^{(0)}$ is the generalized dominant contribution corresponding to the properties of a simple fluid ($\omega = 0$), and $Z^{(1)}$ is a generalized correction function. Extension to mixtures follows a procedure described by Plöcker et al. [95] (see also p. 84).

2. BWRS. A modification of the Benedict-Webb-Rubin equation of state proposed by Starling [115] in which all 11 coefficients are generalized as functions of T_c, ρ_c (critical density), and an acentric factor. Extension to mixtures follows from mixing rules that give the coefficients as functions of mole fraction.

3. RKS. Soave's [114] modification of the Redlich-Kwong equation of state is

$$Z = \frac{V}{V - b} - \frac{a}{RT} \left(\frac{1}{V + b} \right) \tag{8-12.11}$$

where constant b is found from the critical pressure and temperature and "constant" a is a function of reduced temperature and acentric factor:

$$a = \frac{0.42748 R^2 T_c^2}{P_c} [1 + m(1 - \sqrt{T/T_c})]^2 \tag{8-12.12}$$

$$m = 0.48 + 1.574\omega - 0.176\omega^2 \tag{8-12.13}$$

Extension to mixtures is achieved with mixing rules which give a and b as simple functions of mole fraction.

4. PR. Peng and Robinson [90] proposed an equation of state similar to that of Redlich and Kwong:

$$Z = \frac{V}{V - b} - \frac{a}{RT} \left[\frac{1}{(V + b) + (b/V)(V - b)} \right] \tag{8-12.14}$$

Constant b is found from the critical pressure and temperature, and "constant" a depends on reduced temperature and acentric factor:

$$a = \frac{0.45724R^2T_c^2}{P_c} [1 + \chi (1 - \sqrt{T/T_c})]^2 \tag{8-12.15}$$

$$\chi = 0.37464 + 1.54266\omega - 0.26992\omega^2 \tag{8-12.16}$$

Extension to mixtures is the same as that in the RKS equation of state.

All four of these equations of state require essentially the same input parameters: for each pure fluid, critical properties and acentric factors, and for each binary mixture, one binary parameter, designated in this chapter by K_{ij} for LKP and by k_{ij} for the others.† For simple mixtures, K_{ij} is close to unity and k_{ij} is close to zero.

To determine binary parameters, Knapp et al. fit calculated vapor-liquid equilibria to experimental ones. The optimum binary parameter is the one which minimizes DP/P defined by

$$\frac{DP}{P} = \frac{100}{N} \sum_{n=1}^{N} \frac{|P_n^e - P_n^c|}{P_n^e} \tag{8-12.17}$$

where P_n^e is the experimental total pressure of point n and P_n^c is the corresponding calculated total pressure, given temperature T and liquid phase mole fraction x. The total number of experimental points is N.

Similar definitions hold for Dy_1/y_1 and for DK_1/K_1. Here y_1 is the vapor phase mole fraction and K_1 is the K factor ($K_1 = y_1/x_1$) for the more volatile component. In addition, Knapp et al. calculated Df/f by

$$\frac{Df}{f} = \frac{100}{N} \sum_{n=1}^{N} \frac{|f_{1n}^V - f_{1n}^L|}{f_{1n}^V} \tag{8-12.18}$$

where f_1^V is the calculated fugacity of the more volatile component in the vapor phase and f_1^L is that in the liquid phase.

When the binary parameter is obtained by minimizing DP/P, the other deviation functions are usually close to their minima. However, for a given set of data, it is unavoidable that the optimum binary parameter depends somewhat on the choice of objective function for minimization. Minimizing DP/P is preferred because that objective function gives the sharpest minimum and pressures are usually measured with better accuracy than compositions.

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†In the original publication by Plöcker, the binary parameter is designated K_{ij}. In Knapp's monograph, it is designated by k_{ij}^*. In Chap. 4, it is k_w'.

Tables 8-26 and 8-27 show some results reported by Knapp et al. Table 8-26, for propylene-propane, concerns a simple system in which the components are similar; in that case, excellent results are obtained by all four equations of state with only very small corrections to the geometric mean assumption for the characteristic potential energy of a dissimilar pair.

However, calculated results are not nearly as good for the system nitrogen-isopentane. Corrrections to the geometric mean assumption are now appreciable, but, even with such corrections, calculated and observed K factors for nitrogen disagree by about 6 percent for LKP, RKS, and PR and by nearly 12 percent for BWRS.

These two examples illustrate the range of results obtained by Knapp et al. for binary mixtures containing nonpolar components. (Disagreement between calculated and observed vapor-liquid equilibria is often larger when polar components are present.) For most nonpolar binary mixtures,

TABLE 8-26 Comparison of Calculated and Observed Vapor-Liquid Equilibria for the System Propylene (1)–Propane (2)

(From Monograph by Knapp et al.†)

Temperature range: 310 to 344 K
Pressure range: 13 to 31 bar

Equation of state	Binary constant‡	Percent			
		DP/P	Dy_1/y_1	DK_1/K_1	Df_1/f_1
LKP	$K_{12} = 0.9919$	0.31	0.10	0.38	0.46
BWRS	$k_{12} = 0.0025$	0.55	0.06	0.27	0.46
RKS	$k_{12} = 0$	0.56	0.23	0.61	0.90
PR	$k_{12} = 0.0063$	0.31	0.08	0.40	0.29

†Experimental data (77 points) from Laurence and Swift [66].
‡Binary constants obtained by minimizing DP/P.

TABLE 8-27 Comparison of Calculated and Observed Vapor-Liquid Equilibria for the System Nitrogen (1)–Isopentane (2)

(From Monograph by Knapp et al.†)

Temperature range: 277 to 377 K
Pressure range: 1.8 to 207 bar

Equation of state	Binary constant‡	Percent			
		DP/P	Dy_1/y_1	DK_1/K_1	Df_1/f_1
LKP	$K_{12} = 1.347$	5.14	0.87	6.12	4.99
BWRS	$k_{12} = 0.1367$	12.27	3.73	11.62	10.70
RKS	$k_{12} = 0.0867$	4.29	1.58	6.66	5.78
PR	$k_{12} = 0.0922$	3.93	1.61	5.98	5.26

†Experimental data (47 points) from Krishnan et al. [64].
‡Binary constants obtained by minimizing DP/P.

the accuracy of calculated results falls between the limits indicated by Tables 8-26 and 8-27.

While Knapp et al. found overall that the BWRS equation did not perform as well as the others, it is not possible to conclude that, of the four equations used, one particular equation is distinctly superior to the others. Further, it is necessary to keep in mind that the quality of experimental data varies appreciably from one set of data to another. Therefore, if calculated results disagree significantly with experimental ones, one must not immediately conclude that the disagreement is due to a poor equation of state.

Knapp's monograph is limited to binary mixtures. If pure component equation-of-state constants are known and if the mixing rules for these constants are simple, requiring only characteristic binary parameters, then it is possible to calculate vapor-liquid equilibria for ternary (and higher) mixtures by using only pure component and binary data. Although few systematic studies have been made, it appears that this "scale-up" procedure usually provides good results for vapor-liquid equilibria, especially in nonpolar systems. (However, this scale-up procedure is usually not successful for ternary liquid-liquid equilibria, unless special precautions are observed.)

Regardless of what equation of state is used, it is usually worthwhile to make an effort to obtain the best possible equation-of-state constants for the fluids that comprise the mixture. Such constants can be estimated from critical data, but it is usually better to obtain them from vapor pressure and density data as discussed, for example, by Panagiotopoulos and Kumar (88a).

Although Knapp's monograph is concerned with several popular equations of state, it is sometimes useful for special applications to modify one of the standard equations of state. A particularly useful example is provided by Turek et al. [125], who used a modified Redlich-Kwong equation to correlate phase behavior in carbon dioxide–hydrocarbon systems for miscible enhanced oil recovery.

For a pure component, the equation of state is

$$P = \frac{RT}{V - b} - \frac{a}{T^{1/2} V(V + b)} \tag{8-12.19}$$

where V is the molar volume and constants a and b are found from critical pressure P_c and critical temperature T_c:

$$a = \frac{\Omega_a R^2 T_c^{2.5}}{P_c} \tag{8-12.20}$$

$$b = \frac{\Omega_b R T_c}{P_c} \tag{8-12.21}$$

Coefficients Ω_a and Ω_b can be found from the critical condition [$\partial P/\partial V = \partial^2 P/\partial V^2 = 0$ at the critical point] yielding $\Omega_a = 0.42748$ and $\Omega_b = 0.08664$. To improve agreement with experimental vapor pressure, liquid density and supercritical density data, Turek uses slightly temperature-dependent values for Ω_a and Ω_b for carbon dioxide. For hydrocarbons, he establishes generalized relations for Ω_a and Ω_b as functions of reduced temperature and acentric factor.

For a multicomponent mixture M, the composition dependences of constants a and b are given by customary quadratic mixing rules with two adjustable binary parameters, C_{ij} and D_{ij}:

$$a_M = \sum_{i=1} \sum_{j=1} z_i z_j (1 - C_{ij})(a_i a_j)^{1/2} \tag{8-12.22}$$

$$b_M = \tfrac{1}{2} \sum_{i=1} \sum_{j=1} z_i z_j (1 + D_{ij})(b_i + b_j) \tag{8-12.23}$$

where z is the mole fraction ($z_i = y_i$ for the vapor phase and $z_i = x_i$ for the liquid phase) and parameters C_{ij} and $D_{ij} = 0$ whenever $i = j$.

Phase equilibria are related to the equation of state as discussed previously.

Turek et al. reduced extensive binary VLE data to obtain parameters C_{ij} and D_{ij} ($i \neq j$). For hydrocarbon-hydrocarbon pairs, these parameters are small compared to unity; they depend primarily on the molecular size ratio of components i and j. For carbon dioxide–hydrocarbon pairs, parameters C_{ij} and D_{ij} depend on temperature and hydrocarbon acentric factor as shown in Fig. 8-15.

Experimental studies were made for mixtures of carbon dioxide and a synthetic oil whose properties are given in Table 8-28. Experimental K
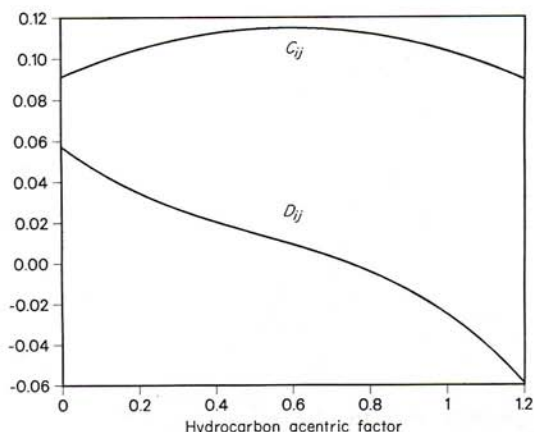

Figure 8-15 Carbon dioxide–hydrocarbon binary interaction parameters.

TABLE 8-28 Composition of Synthetic Oil Used by Turek et al. for Experimental Studies of Vapor-Liquid Equilibria with Carbon Dioxide

Component	Mole percent	Component	Mole percent
Methane	34.67	n-Hexane	3.06
Ethane	3.13	n-Heptane	4.95
Propane	3.96	n-Octane	4.97
n-Butane	5.95	n-Decane	30.21
n-Pentane	4.06	n-Tetradecane	5.04

Density at 322.0 K and 15.48 MPa is 637.0 kg/m^3.
Density at 338.7 K and 14.13 MPa is 613.5 kg/m^3.

factors ($K_i = y_i/x_i$) at 322 K are compared with calculated results in Fig. 8-16. For this case, the modified Redlich-Kwong equation (Amoco Redlich-Kwong), using at most two binary parameters for each binary pair, gives very good agreement with experimental data. (For many of the binary hydrocarbon-hydrocarbon pairs, one or both of the binary parameters can be set equal to zero.) This application of a simple equation of state indicates that, when care is taken to represent thermodynamic properties of pure and binary fluids, it is often possible to scale up to multicomponent vapor-liquid equilibria with good accuracy.

A similar successful scale-up has been established by Mollerup [80], who uses the known thermodynamic properties of a reference fluid (meth-
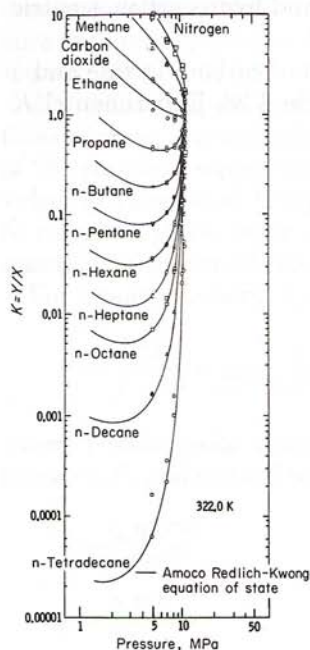
Figure 8-16 K factors for carbon dioxide–synthetic oil.

ane), coupled with pure component and binary parameters, to calculate vapor-liquid equilibria, densities, and enthalpies for natural gas mixtures at low temperatures.

In a typical equation of state, the pressure is given as a function of temperature, volume, and composition. When pressure, temperature, and composition are specified, it is necessary to find the volume. Finding the correct volume is often not simple.

When a single equation of state is used for both liquid and vapor phases, a common pitfall occurs when one is trying to calculate properties for one phase but generates properties for the other. Figure 8-17 shows the phase envelope for an ethane-heptane mixture calculated by the Soave equation (3-6.1). The largest Z value represents a vapor phase: the smallest, a liquid phase. Note that, at low pressures, there is a broad temperature range (and a correspondingly broad range of composition) for which three roots are generated. At higher pressures, this three-root region becomes smaller, and it disappears at the pseudocritical point. Although the behavior in Fig. 8-17 is for the Soave equation, it would be similar for any equation of state. A number of articles have referred to the trivial root problem [19, 28, 45, 96], but the best way to avoid the problem is to make sufficiently accurate initial guesses in iterative calculations. This is illustrated by the following example.

Example 8-12 Estimate the K values for a 26.54% ethane (1)–73.46% heptane (2) mixture at 400 K and 15 bar. This might be the first step in a bubble point pressure calculation with an initial guess of 15 bar.
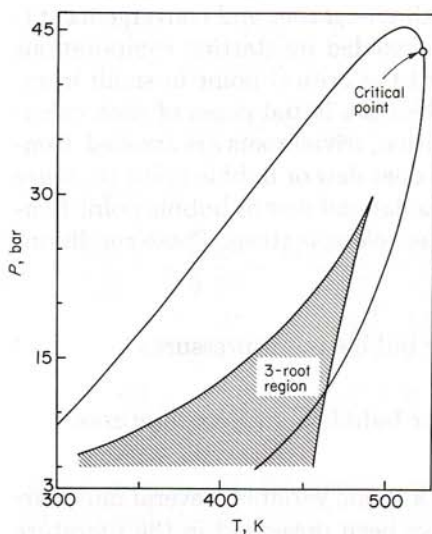

Figure 8-17 Phase envelope calculated by the Soave equation of state for a 26.54% ethane–73.46% n-heptane mixture. In the three-root region, both vapor and liquid properties are calculated.

solution We must make an initial guess for the vapor composition. If we guess y_1 = 0.2654 and y_2 = 0.7346 and use the following properties, Eq. (3-6.2) has only one root, Z = 0.07952.

Compound	T_c, K	P_c, bar	ω
Ethane	305.4	48.8	0.099
Heptane	540.3	27.4	0.349

As expected from Fig. 8-17, this corresponds to a liquid value; K values cannot be calculated because no vapor properties are generated. We need to make an initial guess more likely to generate a vapor phase, for example, y_1 = 0.9 and y_2 = 0.1. Now Eq. (3-6.2) must be solved twice, once with constants from the liquid mole fractions and once with vapor phase constants. Even though both solutions fall in the one root region, the following liquid and vapor properties are generated. Values of ϕ_i are from Eq. (5-8.12).

	Mole fraction of 1	Z	ϕ_1	ϕ_2
Liquid	0.2654	0.07952	5.378	0.1484
Vapor	0.9	0.9327	0.9607	0.7377

$$K_1 = 5.378/0.9607 = 5.598$$
$$K_2 = 0.1484/0.7377 = 0.2012$$

Phase envelope construction—dew and bubble point calculations

Calculations at low pressures present little difficulty, but high-pressure calculations can be complicated by both trivial root and convergence difficulties. Trivial root problems can be avoided by starting computations at a low pressure and marching toward the critical point in small increments of temperature or pressure. When the initial guess of each calculation is the result of a previous calculation, trivial roots are avoided. Convergence difficulties are avoided if one does dew or bubble point *pressure* calculations when the phase envelope is flat and dew or bubble point *temperature* calculations when the phase envelope is steep. These conditions have been stated [139] as follows

If $\left| \dfrac{d \ln P}{d \ln T} \right| < 2$, calculate dew or bubble point pressures

If $\left| \dfrac{d \ln P}{d \ln T} \right| > 20$, calculate dew or bubble point temperatures.

This technique allows convergence on a single variable. Several multivariable Newton-Raphson techniques have been presented in the literature

[8,77]. The advantage of these techniques is that fewer iterations are required for calculations near the critical point (within several degrees or bars). Calculation of dew and bubble points by any method near the critical point is tedious, and although the above methods are often successful, the most efficient approach is to calculate the critical point by the direct method outlined in Sec. 5-6.

To calculate dew or bubble points, values of derivatives must be determined for temperature or pressure adjustment. These derivatives may be determined numerically, or, for the Soave equation, the following expressions may be used.

$$\frac{\partial K_i}{\partial \theta} = K_i \left(\frac{\partial \ln \phi_i^L}{\partial \theta} - \frac{\partial \ln \phi_i^V}{\partial \theta} \right) \tag{8-12.24}$$

where θ may be T or P. For $\theta = T$,

$$\frac{\partial \ln \phi_i}{\partial T} = \frac{b_i}{b} \frac{\partial Z}{\partial T} + \frac{\partial Z/\partial T + B^*/T}{B^* - Z} + \frac{A^*}{Z + B^*} \left(\delta_i - \frac{b_i}{b} \right)$$

$$\times \left(\frac{1}{Z} \frac{\partial Z}{\partial T} + \frac{1}{T} \right) + \left(\frac{b_i}{b} - \delta_i \right) \left(\frac{\partial A^*}{\partial T} + \frac{A^*}{T} \right)$$

$$\times \frac{\ln (1 + B^*/Z)}{B^*} - \frac{A^*}{B^*} \left[\left(\frac{1}{a_i^{1/2}} \frac{\partial a_i^{1/2}}{\partial T} - \frac{1}{a} \frac{\partial a}{\partial T} \right) \delta_i \right.$$

$$\left. + \frac{2a_i^{1/2}}{a} \sum_j x_j (1 - k_{ij}) \frac{\partial a_j^{1/2}}{\partial T} \right] \ln \left(1 + \frac{B^*}{Z} \right) \tag{8-12.25}$$

$$\frac{\partial Z}{\partial T} = \frac{(\partial A^*/\partial T)(B^* - Z) - B^*(A^* + Z + 2B^*Z)/T}{3Z^2 - 2Z + (A^* - B^* - B^{*2})} \tag{8-12.26}$$

$$\frac{\partial A^*}{\partial T} = A^* \left(\frac{1}{a} \frac{\partial a}{\partial T} - \frac{2}{T} \right) \tag{8-12.27}$$

$$\frac{\partial a_i^{1/2}}{\partial T} = -R \frac{fw_i}{2} \left(\frac{0.42748 T_{c_i}}{T P_{c_i}} \right)^{1/2} \tag{8-12.28}$$

For $\theta = P$,

$$\frac{\partial \ln \phi_i}{\partial P} = \frac{b_i}{b} \frac{\partial Z}{\partial P} + \frac{(\partial Z/\partial P) - (B^*/P)}{B^* - Z} \tag{8-12.29}$$

$$+ \frac{A^*}{Z + B^*} \left(\delta_i - \frac{b_i}{b} \right) \left(\frac{1}{Z} \frac{\partial Z}{\partial P} - \frac{1}{P} \right) \tag{8-12.30}$$

$$\frac{\partial Z}{\partial P} = \frac{B^* (2A^* + 2B^*Z + Z) - A^*Z}{P (3Z^2 - 2Z + A^* - B^* - B^{*2})}$$

where a_i, a, b_i, A^*, B^*, and fw_i are given on pages 42 and 43 and in Eqs. (4-5.1) and (4-5.2); $\partial a/\partial T$ is given in Table 5-1; δ_i is given in Table 5-13.

Dew point example

Example 8-13 Use the Soave equation to calculate the dew point temperature at 40 bar for a 26.54% ethane–73.46% heptane mixture.

solution By using the pure component properties in Example 8-12, dew points may be calculated at 5-bar intervals from 5 to 35 bar and then at 1-bar intervals from 35 to 39 bar. The dew point at 39 bar is 521.07 K and $x_1 = 0.1818$. This is used as the initial guess for the dew point calculation at 40 bar. When T is adjusted according to Newton's method and a convergence criterion that $\Sigma y_i/K_i < 1 \times 10^{-8}$ is used, 20 iterations are required. The answer is

$$T = 521.54 \text{ K} \qquad x_1 = 0.1944$$

Note that, in Example 8-12, the cricondentherm would be identified as the point where $\partial \ln P/\partial \ln T$ changes sign. (This occurs at 41.4 bar and 521.81 K.)

Flash example

Example 8-14 For a mixture of 26.54 mole percent ethane and 73.46 mole percent n-heptane at 10 bar and 430 K, calculate the fraction of liquid and the composition of the vapor and liquid phases. Use the Soave equation of state.

solution Use the pure component properties listed in Example 8-12. The following procedure leads to the solution:

1. Guess $L = 0.5$ and $x_i = y_i = z_i$ ($z_i \equiv$ overall mole fraction of i; $L =$ fraction liquid).
2. Solve Eq. (3-6.2) for Z^L and Z^V.
3. Calculate ϕ_i^L and ϕ_i^V with Eq. (5-8.12).
4. Calculate K_i with $K_i = \phi_i^L/\phi_i^V$.
5. See if $\sum_i (x_i - y_i) = 0$, where $x_i = z_i/[K_i + L(1 - K_i)]$ and $y_i = K_i x_i$.
6. If $\sum_i (x_i - y_i)$ is not zero, adjust L according to (King)†

$$L_{new} = L_{old} - \frac{\sum_i \{[z_i(K_i - 1)]/[K_i + (1 - K_i)L]\}}{\sum_i \{[z_i(K_j - 1)^2]/[K_i + (1 - K_i)L]^2\}}$$

7. Go back to step 2 and keep going until $\sum_i (x_i - y_i)$ is zero.

This procedure leads to the following answers:

$L = 0.545$	x_i	y_i	K_i
Ethane	0.0550	0.518	9.410
Heptane	0.9450	0.482	0.5106

---

†C. J. King, *Separation Processes*, 2d ed. McGraw-Hill, New York, 1980, pp. 64–80.

For the above procedure, 10 iterations were required to obtain the condition that

$$\left| \sum_i (y_i - x_i) \right| < 10^{-8}$$

Although well-known equations of state (e.g., Redlich-Kwong-Soave and Peng-Robinson) are suitable for calculating vapor-liquid equilibria for nonpolar mixtures, these equations of state, using conventional mixing rules, are not satisfactory for mixtures containing strongly polar and hydrogen-bonded fluids in addition to the common gases and hydrocarbons. For those mixtures, the assumption of simple (random) mixing is poor because strong polarity and hydrogen bonding can produce significant segregation or ordering of molecules in mixtures. For example, at ordinary temperatures, water and benzene form a strongly nonrandom mixture; the mixture is so far from random that water and benzene are only partially miscible at ordinary temperatures because preferential forces of attraction between water molecules tend to keep these molecules together and prevent their random mixing with benzene molecules.

It is possible to describe deviations from simple mixing by using complex (essentially empirical) mixing rules, as shown, for example, by Vidal [127]. For thermodynamic consistency, however, these mixing rules must be density-dependent because at low densities, the equation of state must give a second virial coefficient which is quadratic in mole fraction. The common mixing rules satisfy that boundary condition, but the mixing rules of Vidal (which are independent of density) do not. Some early work on density-dependent mixing rules has been reported by Whiting and Prausnitz [129], Mollerup [81], Mathias and Copeman [74], and by Won [134], and some promising results have been achieved for binary mixtures. Panagiotopoulos and Reid [88b] have reported practical application to ternary systems containing two liquid phases.

A useful technique for describing nonrandom fluid mixtures is provided by the chemical hypothesis which postulates the existence of various chemical species formed by the nominal components. For example, a mixture of fluids A and B is assumed to contain not only monomers A and B but, in addition, dimers, trimers, etc., of A and of B and, further, complexes of A and B with the general formula $A_n B_m$, where n and m are positive integers. Concentrations of the various chemical species are found from chemical equilibrium constants coupled with material balances.

The chemical hypothesis was used many years ago to calculate activity coefficients in liquid mixtures and also to calculate second virial coefficients of pure and mixed gases. However, the early work was restricted to liquids or to gases at moderate densities, and most of that early work assumed that the "true" chemical species form ideal mixtures. It was not until 1976 that Heidemann [51] combined the chemical hypothesis with

an equation of state valid for all fluid densities. Unfortunately, Heidemann's work is limited to pure fluids; for extension to mixtures additional assumptions are required as discussed by Hu et al. [58]. However, the chemical hypothesis, coupled with an equation of state, becomes tractable for mixtures provided that association is limited to dimers as shown in 1979 by Gmehling et al. Since then, several other authors have presented similar ideas.

Gmehling et al. [42] used an equation of state of the van der Waals form (in particular, the perturbed-hard-chain equation of state) coupled with a dimerization hypothesis. A binary mixture of nominal components A and B is considered to be a five-species mixture containing two types of monomer (A_1 and B_1) and three types of dimer (A_2, B_2, AB).

There are three chemical equilibrium constants:

$$K_{A_2} = \frac{z_{A_2}}{z_{A_1}^2} \frac{\phi_{A_2}}{\phi_{A_1}^2} \frac{1}{P} \tag{8-12.31a}$$

$$K_{B_2} = \frac{z_{B_2}}{z_{B_1}^2} \frac{\phi_{B_2}}{\phi_{B_1}^2} \frac{1}{P} \tag{8-12.31b}$$

$$K_{AB} = \frac{z_{AB}}{z_{A_1}z_{B_1}} \frac{\phi_{AB}}{\phi_{A_1}\phi_{B_1}} \frac{1}{P} \tag{8-12.31c}$$

where z_{A_1} is the mole fraction of A_1 (etc.) and ϕ_{A_1} is the fugacity coefficient of A_1 (etc.). The fugacity coefficient is found from the equation of state by using physical interaction parameters to characterize monomer-monomer, monomer-dimer, and dimer-dimer interactions.

Mole fractions z are related to nominal mole fractions x_A and x_B through chemical equilibrium constants and material balances.

To reduce the number of adjustable parameters, Gmehling established physically reasonable relations between parameters for monomers and those for dimers.

The temperature dependence of equilibrium constant K_{A_2} is given by

$$\ln K_{A_2} = \frac{\Delta H_{A_2}^\circ}{RT} + \frac{\Delta S_{A_2}^\circ}{R} \tag{8-12.32}$$

where $\Delta H_{A_2}^\circ$ is the enthalpy and $\Delta S_{A_2}^\circ$ is the entropy of formation of dimer A_2 in the standard state. Similar equations hold for K_{B_2} and K_{AB}.

All pure component parameters (including K_{A_2} and K_{B_2}) are obtained from experimental density and vapor pressure data.

A reasonable estimate for ΔH_{AB}° is provided by

$$\Delta H_{AB}^\circ = \tfrac{1}{2}(\Delta H_{A_2}^\circ + \Delta H_{B_2}^\circ) \tag{8-12.33}$$

but a similar relation of ΔS°_{AB} does not hold. For a binary mixture of A and B, ΔS°_{AB} must be found from binary data.

The equations for vapor-liquid equilibrium are

$$f_A^V = f_A^L \quad \text{and} \quad f_B^V = f_B^L \tag{8-12.34}$$

where f stands for fugacity and superscripts V and L stand for vapor and liquid, respectively. As shown in Ref. 103, chap. 26, Eq. (8-12.34) can be replaced without loss of generality by

$$f_{A_1}^V = f_{A_1}^L \quad \text{and} \quad f_{B_1}^V = f_{B_1}^L \tag{8-12.35}$$

Figure 8-18 shows calculated and observed vapor-liquid equilibria for methanol-water at modest and advanced pressures. Calculations are based on Gmehling's equation as outlined above. For this mixture, the calculations require only two adjustable binary parameters which are independent of temperature over the indicated temperature range. One of these is ΔS°_{AB}, and the other is $k_{A_1-B_1}$, a physical parameter to characterize $A_1 - B_1$ interactions.
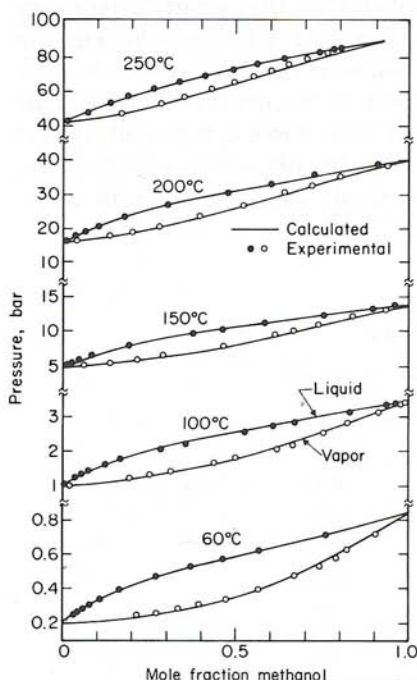

Figure 8-18 Vapor-liquid equilibria for methanol-water.

Gmehling's equation of state, coupled with a (chemical) dimerization hypothesis, is particularly useful for calculating vapor-liquid equilibria at high pressures for fluid mixtures containing polar and nonpolar components, some subcritical and some supercritical. By using an equation of state valid for both phases, the equations of phase equilibrium avoid the awkward problem of defining a liquid phase standard state for a supercritical component. By superimposing dimerization equilibria onto a "normal" equation of state, Gmehling achieves good representation of thermodynamic properties for both gaseous and liquid mixtures containing polar or hydrogen-bonded fluids in addition to "normal" fluids (such as common gases and hydrocarbons) by using the same characteristic parameters for both phases.

Buck [24] tested Gmehling's method by comparing calculated and observed vapor-liquid equilibria for several ternary systems containing polar and hydrogen-bonded fluids. Encouraged by favorable comparisons, Buck then describes an application of Gmehling's method to an isothermal flash calculation at 200°C and 100 bar. Table 8-29 shows specified feed compositions and calculated compositions for the vapor and for the liquid at equilibrium. All required parameters were obtained from pure component and binary experimental data.

To implement Gmehling's method for multicomponent fluid mixtures, it is necessary to construct a far-from-trivial computer program requiring a variety of iterations. The calculations summarized in Table 8-29 are for seven components, but the number of (assumed) chemical species is much larger. For H_2, CO, and CH_4 it is reasonable to assume that no dimers are formed; further, it is reasonable to assume that these components do not form cross-dimers with each other or with the other components in the mixture. However, the four polar components form dimers with them-

TABLE 8-29 Isothermal Flash Calculation Using Gmehling's Equation of State at 200°C and 100 bar [24]

Component	Feed	Vapor	Liquid
	Mole percent of		
Hydrogen	6.0	33.86	2.03
Carbon monoxide	5.5	24.63	2.77
Methane	0.3	1.08	0.19
Methyl acetate	27.2	13.34	29.18
Ethanol	39.9	19.35	42.83
Water	3.3	1.81	3.51
1,4-Dioxane	17.8	5.93	19.49
Total moles	100.00	12.49	87.51

selves and with each other. In Gmehling's method, therefore, this 7-component mixture is considered to be a mixture of 17 chemical species.

Example 8-15 Use Gmehling's method to calculate the bubble point pressure and vapor phase composition for a mixture of 4.46 mole percent methanol (1) and 95.54 mole percent water (2) at 60°C.

solution In the Gmehling model, a water-methanol mixture contains five species: methanol and water monomers, methanol dimers, water dimers, and a methanol-water cross-dimer. The mole fractions of these are, respectively, z_{M1}, z_{M2}, z_{D1}, z_{D2}, and z_{D12}. There are 13 unknowns and 13 equations. The unknowns include five liquid z values, five vapor z values, and the pressure and molar volumes, of the liquid and vapor phases. The 13 equations are the equation of state for both the liquid and vapor phases, the three reaction equilibrium equations (8-12.31a) through (8-12.31c), five fugacity equalities (that is, $f_i^L = f_i^V$), $\Sigma z_i = 1$ in both the liquid and vapor, and a material balance accounting for the mixture composition. Pure component parameters from [42] are as follows:

Component	T^*, K	V^*, cm³/mol	$\Delta S°/R$	$\Delta H°R$, K
Methanol (1)	348.09	26.224	−16.47	−5272
Water (2)	466.73	12.227	−14.505	−4313

From Eq. (8-12.32),

$$K_1 = \exp\left(-16.47 + \frac{5272}{333.15}\right) = 0.525$$

Similarly, $K_2 = 0.210$
From [42], $\Delta S°_{12}/R = -15.228$ and $k_{12} = 0.0371$ and $K_{12} = \exp\left(-15.228 + \dfrac{(5272 + 4313)(0.5)}{333.15}\right) = 0.431$

The problem may be solved by the following procedure:

1. Guess P.
2. Guess all $\phi_i = 1$.
3. Guess $y_i = x_i$.
4. Solve the reaction equilibria problem for values of z_i in each phase [Eqs. (8-12.31a) to (8-12.31c)].
5. Calculate mixture parameters with mixing rules from [42].
6. Solve the equation of V^L and V^V.
7. Calculate ϕ_i for each of the five species in both phases.
8. Go back to step 4 and recalculate z_i values. When z_i values no longer change, reaction equilibria are satisfied, but phase equilibria are not.
9. Calculate K_i by $K_i = \phi_i^L/\phi_i^V$, where $K_i \equiv z_i^V/z_i^L$.
10. See if $\sum_i K_i z_i^L = 1$; if not, adjust P according to $P_{new} = P_{old}\left(\sum_i K_i z_i^L\right)$ and go back to step 4.

This procedure converges to the following values:

	z_{M1}	z_{M2}	z_{D1}	z_{D2}	z_{D12}	V
Liquid	0.001680	0.05252	0.003510	0.8642	0.07808	0.03706
Vapor	0.2641	0.6794	0.00980	0.02603	0.0207	103.3

	ϕ_{M1}	ϕ_{M2}	ϕ_{D1}	ϕ_{D2}	ϕ_{D12}
Liquid	156.6	12.91	2.775	0.02996	0.2636
Vapor	0.9976	0.9983	0.9937	0.9947	0.9942

$P = 0.2675$ bar

The above numbers satisfy the material balance and reaction equilibria equations:

$$x_1 = \frac{z_{M1}^L + 2z_{D1}^L + z_{D12}^L}{z_{M1}^L + z_{M2}^L + 2(z_{D1}^L + z_{D12}^L + z_{D2}^L)}$$

$$= \frac{0.00168 + (2)(0.00351) + 0.0781}{0.00168 + 0.0525 + (2)(0.00351 + 0.864 + 0.0781)} = 0.0446$$

$$K_1 = \frac{z_{D1}\phi_{D1}}{z_{M1}^2\phi_{M1}^2}\frac{1}{P} = \frac{0.00351}{(0.00168)^2}\frac{2.775}{(156.6)^2}\frac{1}{0.2675} = 0.526$$

$$K_{12} = \frac{z_{D12}}{z_{M1}z_{M2}}\frac{\phi_{D12}}{\phi_{M1}\phi_{M2}}\frac{1}{P} = \frac{0.07808}{(0.00168)(0.05252)}\frac{(0.2336)}{(156.6)(12.91)}\frac{1}{0.2675} = 0.431$$

$$K_2 = \frac{z_{D2}}{z_{M2}^2}\frac{\phi_{D2}}{\phi_{M2}^2}\frac{1}{P} = \frac{0.8642}{(0.05252)^2}\frac{0.02996}{(12.91)^2}\frac{1}{0.2675} = 0.210$$

The reaction expressions are verified above for liquid phase values. They are also satisfied for vapor phase values, since $f_i^L = f_i^V$ is satisfied for each of the five components (as can easily be verified). Mixture parameters to be used can be obtained from mixing rules in [42]. For example, for the liquid phase,

$$
\begin{aligned}
<cT^*V^*> &= z_{M1}c_{M1}T_{M1}^*\,[z_{M1}V_{M1}^* + z_{M2}V_{M2}^*(1-k_{12}) + z_{D1}V_{D1}^* + z_{D2}V_{D2}^*(1-k_{12}) \\
&\quad + z_{D12}V_{D12}^*(1-k_{12})^{1/2} + z_{M2}c_{M2}T_{M2}^*(z_{M1}V_{M1}^*(1-k_{12}) + z_{M2}V_{M2}^* \\
&\quad + z_{D1}V_{D1}^*(1-k_{12}) \\
&\quad + z_{D2}V_{D2}^* + z_{D12}V_{D12}^*(1-k_{12})^{1/2}] + z_{D1}c_{D1}T_{D1}^*[z_{M1}V_{M1}^* \\
&\quad + z_{M2}V_{M2}^*(1-k_{12}) + z_{D1}V_{D1}^* + z_{D2}V_{D2}^*(1-k_{12}) \\
&\quad + z_{D12}V_{D12}^*(1-k_{12})^{1/2}] + z_{D2}c_{D2}T_{D2}^*[z_{M1}V_{M1}^*(1-k_{12}) \\
&\quad + z_{M2}V_{M2}^* + z_{D1}V_{D1}^*(1-k_{12}) + z_{D2}V_{D2}^* \\
&\quad + z_{D12}V_{D12}^*(1-k_{12})^{1/2}] + z_{D12}c_{D12}T_{D12}^*[z_{M1}V_{M1}^*(1-k_{12})^{1/2} \\
&\quad + z_{M2}V_{M2}^*(1-k_{12})^{1/2} + z_{D1}V_{D1}^*(1-k_{12})^{1/2} \\
&\quad + z_{D2}V_{D2}^*(1-k_{12})^{1/2} + z_{D12}V^*_{D12}(1-k_{12})^{1/2}] \\
&= 12 + 537 + 45 + 15465 + 1200 \\
<cT^*V^*> &= 17{,}259 \ (\text{K}\cdot\text{cm}^3)/\text{mol}
\end{aligned}
$$

Values of all parameters as as follows:

	$<c>$	$<V^*>$	$<cT^*V^*>$	$<T^*>^{(2)}$
Vapor	1.017	16.93	7503	444.92
Liquid	1.284	21.97	17259	614.72

As the last step, values of y_i and V in moles per liter of original monomer may be calculated:

$$y_1 = \frac{z^V_{M1} + 2z^V_{D1} + z^V_{D12}}{z^V_{M1} + z^V_{M2} + 2(z^V_{D1} + z^V_{D2} + z^V_{D12})} = 0.2881$$

$$y_2 = 0.7119$$

$$V^V = \frac{103.3}{z^V_{M1} + z^V_{M2} + 2(z^V_{D1} + z^V_{D2} + z^V_{D12})} = 97.8 \text{ mol/L}$$

$$V^L = \frac{0.03706}{z^L_{M1} + z^L_{M2} + 2(z^L_{D1} + z^L_{D2} + z^L_{D12})} = 0.01905 \text{ mol/L}$$

Experimental values are $P = 0.2625$ bar and $y_1 = 0.2699$.

8-13 Liquid-Liquid Equilibria

Many liquids are only partially miscible, and in some cases, e.g., mercury and hexane at normal temperatures, the mutual solubilities are so small that, for practical purposes, the liquids may be considered immiscible. Partial miscibility is observed not only in binary mixtures but also in ternary (and higher) systems, thereby making extraction a possible separation operation. This section introduces some useful thermodynamic relations which, in conjunction with limited experimental data, can be used to obtain quantitative estimates of phase compositions in liquid-liquid systems.

At ordinary temperatures and pressures, it is (relatively) simple to obtain experimentally the compositions of two coexisting liquid phases, and, as a result, the technical literature is rich in experimental results for a variety of binary and ternary systems near 25°C and near atmospheric pressure. However, as temperature and pressure deviate appreciably from those corresponding to normal conditions, the availability of experimental data falls rapidly.

Partial miscibility in liquids is often called *phase splitting*. The thermodynamic criteria which indicate phase splitting are well understood regardless of the number of components [79], but most thermodynamic texts confine discussion to binary systems. Stability analysis shows that, for a binary system, phase splitting occurs when

$$\left(\frac{\partial^2 g^E}{\partial x_1^2}\right)_{T,P} + RT\left(\frac{1}{x_1} + \frac{1}{x_2}\right) < 0 \tag{8-13.1}$$

where g^E is the molar excess Gibbs energy of the binary mixture (see Sec. 8-5). To illustrate Eq. (8-13.1), consider the simplest nontrivial case. Let

$$g^E = Ax_1x_2 \tag{8-13.2}$$

where A is an empirical coefficient characteristic of the binary mixture. Substituting into Eq. (8-13.1), we find that phase splitting occurs if

$$A > 2RT \tag{8-13.3}$$

In other words, if $A < 2RT$, the two components 1 and 2 are completely miscible; there is only one liquid phase. However, if $A > 2RT$, two liquid phases form because components 1 and 2 are only partially miscible.

The condition in which $A = 2RT$ is called *incipient instability,* and the temperature corresponding to that condition is called the *consolute temperature,* designated by T^c. Since Eq. (8-13.2) is symmetric in mole fractions x_1 and x_2, the composition at the consolute point is $x_1^c = x_2^c = 0.5$. In a typical binary mixture, the coefficient A is a function of temperature, and therefore it is possible to have either an upper consolute temperature or a lower consolute temperature, or both, as indicated in Figs. 8-19 and 8-20. Upper consolute temperatures are more common than lower consolute temperatures. Systems with both upper and lower consolute temperatures are rare.†
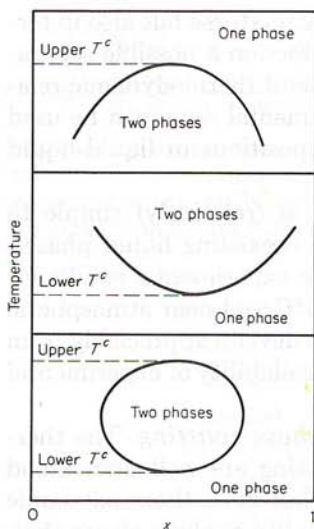

Figure 8-19 Phase stability in three binary liquid mixtures. *(From Ref. 97.)*

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†Although Eq. (8-13.3) is based on the simple two-suffix (one-parameter) Margules equation, similar calculations can be made using other expressions for g^E. See, for example, Ref. 111.
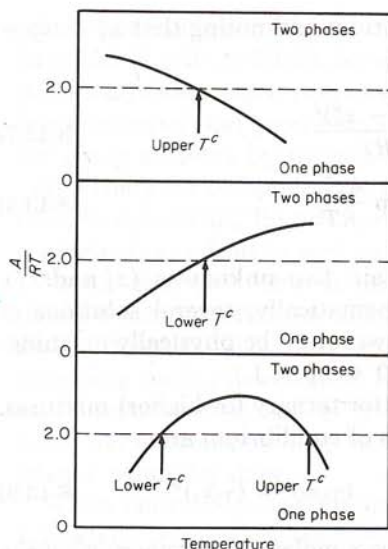
Figure 8-20 Phase stability in three binary liquid mixtures whose excess Gibbs energy is given by a two-suffix Margules equation. *(From Ref. 97.)*

Stability analysis for ternary (and higher) systems is, in principle, similar to that for binary systems, although the mathematical complexity rises with the number of components. (See, for example, Refs. 14 and 103.) However, it is important to recognize that stability analysis can tell us only whether a system can or cannot *somewhere* exhibit phase splitting at a given temperature. That is, if we have an expression for g^E at a particular temperature, stability analysis can determine whether or not there is *some* range of composition where two liquids exist. It does *not* tell us what that compositon range is. To find the range of compositions in which two liquid phases exist at equilibrium requires a more elaborate calculation. To illustrate, consider again a simple binary mixture whose excess Gibbs energy is given by Eq. (8-13.2). If $A > 2RT$, we can calculate the compositions of the two coexisting equations by solving the two equations of phase equilibrium

$$(\gamma_1 x_1)' = (\gamma_1 x_1)'' \quad \text{and} \quad (\gamma_2 x_2)' = (\gamma_2 x_2)'' \tag{8-13.4}$$

where the prime and double prime designate, respectively, the two liquid phases.

From Eq. (8-13.2) we have

$$\ln \gamma_1 = \frac{A}{RT} x_2^2 \tag{8-13.5}$$

and

$$\ln \gamma_2 = \frac{A}{RT} x_1^2 \tag{8-13.6}$$

Substituting into the equation of equilibrium and noting that $x_1' + x_2' = 1$ and $x_1'' + x_2'' = 1$, we obtain

$$x_1' \exp \frac{A(1 - x_1')^2}{RT} = x_1'' \exp \frac{A(1 - x_1'')^2}{RT} \tag{8-13.7}$$

and

$$(1 - x_1') \exp \frac{Ax_1'^2}{RT} = (1 - x_1'') \exp \frac{Ax_1''^2}{RT} \tag{8-13.8}$$

Equations (8-13.7) and (8-13.8) contain two unknowns (x_1' and x_1''), which can be found by iteration. Mathematically, several solutions of these two equations can be obtained. However, to be physically meaningful, it is necessary that $0 < x_1' < 1$ and $0 < x_1'' < 1$.

Similar calculations can be performed for ternary (or higher) mixtures. For a ternary system the three equations of equilibrium are

$$(\gamma_1 x_1)' = (\gamma_1 x_1)'' \qquad (\gamma_2 x_2)' = (\gamma_2 x_2)'' \qquad (\gamma_3 x_3)' = (\gamma_3 x_3)'' \tag{8-13.9}$$

If we have an equation relating the excess molar Gibbs energy g^E of the mixture to the overall composition (x_1, x_2, x_3), we can obtain corresponding expressions for the activity coefficients γ_1, γ_2, and γ_3, as discussed elsewhere [see Eq. (8-9.4)]. The equations of equilibrium [Eq. (8-13.9)], coupled with material balance relations, can then be solved to obtain the four unknowns (x_1', x_2' and x_1'', x_2'').

Systems containing four or more components are handled in a similar manner. An expression for g^E for the multicomponent system is used to relate the activity coefficient of each component in each phase to the composition of that phase. From the equations of equilibrium [$(\gamma_i x_i)' = (\gamma_i x_i)''$ for every component i] the phase compositions x_i' and x_i'' are found by trial and error.

Considerable skill in numerical analysis is required to construct a computer program that finds the equilibrium compositions of a multicomponent liquid-liquid system from an expression for the excess Gibbs energy for that system. It is difficult to construct a program which always converges to a physically meaningful solution by using only a small number of iterations. This difficulty is especially pronounced in the region near the plait point, where the compositions of the two equilibrium phases become identical.

King [60] has given some useful suggestions for constructing efficient programs toward computation of equilibrium compositions in two-phase systems. See also Ref. 99.

Although the thermodynamics of multicomponent liquid-liquid equilibria is, in principle, straightforward, it is difficult to obtain an expression for g^E which is sufficiently accurate to yield reliable results. Liquid-liquid equilibria are much more sensitive to small changes in activity coefficients than vapor-liquid equilibria. In the latter, activity coefficients play a role

which is secondary to the all-important pure component vapor pressures. In liquid-liquid equilibria, however, the activity coefficients are dominant; pure component vapor pressures play no role at all. Therefore, it has often been observed that good estimates of vapor-liquid equilibria can be made for many systems by using only approximate activity coefficients, provided the pure component vapor pressures are accurately known. However, in calculating liquid-liquid equilibria, small inaccuracies in activity coefficients can lead to serious errors.

Renon et al [99] have discussed application of the NRTL equation to liquid-liquid equilibria, Anderson and Prausnitz have discussed application of the UNIQUAC equation [6], and there are many other articles providing similar discussions. Regardless of which equation is used, much care must be exercised in determining parameters from experimental data. Whenever possible, such parameters should come from binary mutual solubility data.

When parameters are obtained from reduction of vapor-liquid equilibrium data, there is always some ambiguity. Unless the experimental data are of very high accuracy, it is usually not possible to obtain a truly unique set of parameters; i.e., in a typical case, there is a range of parameter sets such that any set in that range can equally well reproduce the experimental data within the probable experimental error. (See, for example, Refs. 4 and 33.) When multicomponent vapor-liquid equilibria are calculated, results are often not sensitive to which sets of binary parameters are chosen. However, when multicomponent liquid-liquid equilibria are calculated, results are extremely sensitive to the choice of binary parameters. Therefore, it is difficult to establish reliable ternary (or higher) liquid-liquid equilibria by using only binary parameters obtained from binary liquid-liquid and binary vapor-liquid equilibrium data. For reliable results it is usually necessary to utilize at least some multicomponent liquid-liquid equilibrium data.

To illustrate these ideas, we quote some calculations reported by Bender and Block [15], who considered two ternary systems at 25°C:

System I: Water (1), toluene (2), aniline (3)

System II: Water (1), TCE† (2), acetone (3)

To describe these systems, the NRTL equation was used to relate activity coefficients to composition. The essential problem lies in finding the parameters for the NRTL equation. In system I, components 2 and 3 are completely miscible but components 1 and 2 and components 1 and 3 are only partially miscible. In system II, components 1 and 3 and components 2 and 3 are completely miscible but components 1 and 2 are only partially miscible.

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†1,1,2-Trichloroethane.

For the completely miscible binaries, Bender and Block set NRTL parameter $\alpha_{ij} = 0.3$. Parameter τ_{ij} and τ_{ji} were then obtained from vapor-liquid equilibria. Since it is not possible to obtain unique values of these parameters from vapor-liquid equilibria, Bender and Block used a criterion suggested by Abrams and Prausnitz [4], namely, to choose those sets of parameters for the completely miscible binary pairs which correctly give the limiting liquid-liquid distribution coefficient for the third component at infinite dilution. In other words, NRTL parameters τ_{ij} and τ_{ji} chosen were those which not only represent the ij binary vapor-liquid equilibria within experimental accuracy but also give the experimental value of K_k^∞ defined by

$$K_k^\infty = \lim_{\substack{w_j' \to 0 \\ w_k' \to 0}} \frac{w_k''}{w_k'}$$

where w stands for weight fraction, component k is the third component, i.e., the component *not* in the completely miscible ij binary, and the prime and double prime designate the two equilibrium liquid phases.

For the partially miscible binary pairs, estimates of τ_{ij} and τ_{ji} are obtained from mutual-solubility data following an arbitrary choice for α_{ij} in the region $0.20 \leqslant \alpha_{ij} \leqslant 0.40$. When mutual-solubility data are used, the parameter set τ_{ij} and τ_{ji} depends only on α_{ij}; to find the best α_{ij}, Bender and Block used ternary tie-line data. In other words, since the binary parameters are not unique, the binary parameters chosen were those which gave an optimum representation of the ternary liquid-liquid equilibrium data.

Table 8-30 gives mutual solubility data for the three partially miscible binary systems. Table 8-31 gives NRTL parameters following the procedure outlined above. With these parameters, Bender and Block obtained good representation of the ternary phase diagrams, essentially within experimental error. Figures 8-21 and 8-22 compare calculated with observed distribution coefficients for systems I and II.

TABLE 8-30 Mutual Solubilities in Binary Systems at 25°C [15]

Component		Weight fraction	
i	j	i in j	j in i
Water	TCE	0.0011	0.00435
Water	Toluene	0.0005	0.000515
Water	Aniline	0.053	0.0368

TABLE 8-31 NRTL Parameters Used by Bender and Block to Calculate Ternary Liquid-Liquid Equilibria at 25°C

		System I:	water (1), toluene (2), aniline (3)	

i	j	τ_{ij}	τ_{ji}	α_{ij}
1	2	7.77063	4.93035	0.2485
1	3	4.18462	1.27932	0.3412
2	3	1.59806	0.03509	0.3

		System II:	water (1), TCE (2), acetone (3)	

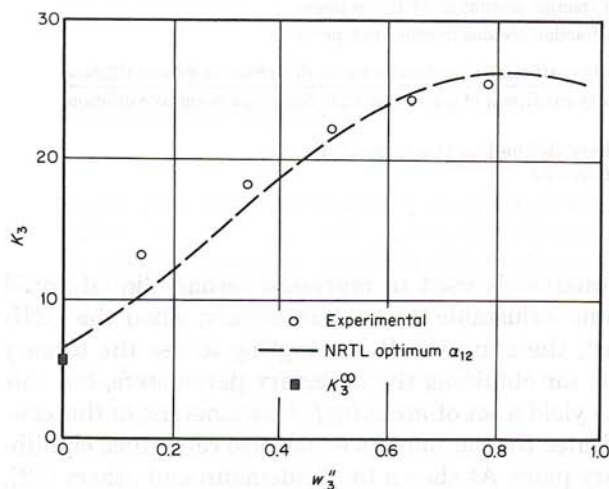| i	j	τ_{ij}	τ_{ji}	α_{ij}
1	2	5.98775	3.60977	0.2485
1	3	1.38800	0.75701	0.3
2	3	− 0.19920	− 0.20102	0.3

Figure 8-21 Distribution coefficient K_3 for the system water (1)–toluene (2)–aniline (3) at 25°C. Concentrations are weight fractions.

$$K_3 = \frac{w_3''}{w_3'} = \frac{\text{weight fraction aniline in toluene-rich phase}}{\text{weight fraction aniline in water-rich phase}}$$

$$K_3^\infty = \frac{\gamma_3'^\infty}{\gamma_3''^\infty} = \frac{\text{activity coefficient of aniline in water-rich phase at infinite dilution}}{\text{activity coefficient of aniline in toluene-rich phase at infinite dilution}}$$

Activity coefficient γ is here defined as the ratio of activity to weight fraction. *(From Ref. 15.)*
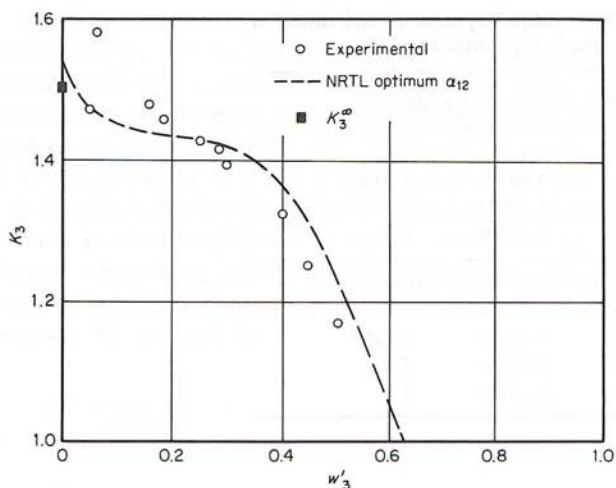
Figure 8-22 Distribution coefficient K_3 for the system water (1)–TCE (2)–acetone (3) at 25°C. Concentrations are in weight fractions.

$$K_3 = \frac{w_3''}{w_3'} = \frac{\text{weight fraction acetone in TCE-rich phase}}{\text{weight fraction acetone in water-rich phase}}$$

$$K_3^\infty = \frac{\gamma'_3{}^\infty}{\gamma''_3{}^\infty} = \frac{\text{activity coefficient of acetone in water-rich phase at infinite dilution}}{\text{activity coefficient of acetone in TCE-rich phase at infinite dilution}}$$

Activity coefficient γ is here defined as the ratio of activity to weight fraction. *(From Ref. 15.)*

When the NRTL equation is used to represent ternary liquid-liquid equilibria, there are nine adjustable binary parameters; when the UNIQUAC equation is used, there are six. It is tempting to use the ternary liquid-liquid data alone for obtaining the necessary parameters, but this procedure is unlikely to yield a set of *meaningful* parameters; in this context "meaningful" indicates the parameters which also reproduce equilibrium data for the binary pairs. As shown by Heidemann and others [52], unusual and bizarre results can be calculated if the parameter sets are not chosen with care. Experience in this field is not yet plentiful, but all indications are that it is always best to use binary data for calculating binary parameters. Since it often happens that binary parameter sets cannot be determined uniquely, ternary (or higher) data should then be used to fix the best binary sets from the ranges obtained from the binary data. (For a typical range of binary parameter sets, see Fig. 8-4.) It is, of course, always possible to add ternary (or higher) terms to the expression for the excess Gibbs energy and thereby introduce ternary (or higher) constants.

This is sometimes justified, but it is meaningful only if the multicomponent data are plentiful and of high accuracy.

In calculating multicomponent equilibria, the general rule is to use binary data first. Then use multicomponent data for fine tuning.

Example 8-16 Acetonitrile (1) is used to extract benzene (2) from a mixture of benzene and n-heptane (3) at 45°C.

(a) 0.5148 mol of acetonitrile is added to a mixture containing 0.0265 mol of benzene and 0.4587 mol of n-heptane to form 1 mol of feed.

(b) 0.4873 mol of acetonitrile is added to a mixture containing 0.1564 mol of benzene and 0.3563 mol of n-heptane to form 1 mol of feed.

For (a) and for (b), find the composition of the extract phase E, the composition of the raffinate phase R and α, and the fraction of feed in the extract phase.

solution To find the desired quantities, we must solve an isothermal flash problem in which 1 mol of feed separates into α mol of extract and $1 - \alpha$ mol of raffinate.

There are five unknowns: 2 mole fractions in E, 2 mole fractions in R, and α. To find these five unknowns, we require five independent equations. They are three equations of phase equilibrium

$$(\gamma_i x_i)^E = (\gamma_i x_i)^R \qquad i = 1, 2, 3$$

and two material balances

$$z_i = x_i^E \alpha + x_i^R (1 - \alpha) \qquad \text{for any two components}$$

Here z_i is the mole fraction of component i in the feed; x^E and x^R are, respectively, mole fractions in E and in R, and γ is the activity coefficient.

To solve five equations simultaneously, we use an iterative procedure based on the Newton-Raphson method as described in Ref. 99. The objective function F is

$$F(x^R, x^E, \alpha) = \sum_{i=1}^{3} \frac{(K_i - 1)z_i}{(K_i - 1)\alpha + 1} \to 0$$

where

$$K_i = \frac{x_i^E}{x_i^R} = \frac{\gamma_i^R}{\gamma_i^E}$$

For activity coefficients, we use the UNIQUAC equation with the following parameters:

Pure Component Parameters

Component	r	q
1	1.87	1.72
2	3.19	2.40
3	5.17	4.40

Binary Parameters

$$\tau_{ij} = \exp\left(-\frac{a_{ij}}{T}\right) \qquad \tau_{ji} = \exp\left(-\frac{a_{ji}}{T}\right)$$

Components		a_{ij}, K	a_{ji}, K
i	j		
1	2	60.28	89.57
1	3	23.71	545.8
2	3	−135.9	245.4

In the accompanying table calculated results are compared with experimental data.†

**Liquid-Liquid Equilibria in the System Acetonitrile (1)–Benzene (2)–
n-Heptane (3) at 45°C**

	i	γ_i^R	$100x_i^R$		γ_i^E	$100x_i^E$	
			Calc.	Exp.		Calc.	Exp.
(a)	1	7.15	13.11	11.67	1.03	91.18	91.29
	2	1.25	3.30	3.41	2.09	1.98	1.88
	3	1.06	83.59	84.92	12.96	6.84	6.83
(b)	1	3.38	25.63	27.23	1.17	73.96	70.25
	2	1.01	18.08	17.71	1.41	12.97	13.56
	3	1.35	56.29	55.06	5.80	13.07	16.19

For (a), the calculated $\alpha = 0.4915$; for (b), it is 0.4781. When experimental data are substituted into the material balance, $\alpha = 0.5$ for both (a) and (b).
In this case, there is good agreement between calculated and experimental results because the binary parameters were selected by using binary and ternary data.

While activity coefficient models are commonly used for liquid-liquid equilibria, it is also possible to use an equation of state to correlate liquid-liquid solubility data, as shown, for example, by Tsonopoulos and Wilson [124], who correlated the solubility of water in hydrocarbons by using a variation of the Redlich-Kwong equation of state proposed by Zudkevitch and Joffe. In this variation, for every pure component, equation-of-state constants are given a temperature dependence such that, for temperatures below the critical, the equation of state correctly reproduces experimental vapor pressures and saturated liquid densities. For binary water-hydrocarbon mixtures, the usual mixing rules were used with an adjustable binary constant to correct for deviations from the geometric mean assumption for cross coefficient $a_{12} = (a_1 a_2)^{1/2}(1 - k_{12})$.

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†Palmer and Smith [88].

To find k_{12} from solubility data, let subscript 1 stand for water and subscript 2 for hydrocarbon. The equation of equilibrium is

$$f_1' = f_1'' \tag{8-13.10}$$

where f is fugacity, prime stands for the water-rich phase, and double prime stands for the hydrocarbon-rich phase.

For f_1' we write

$$f_1' = f_{\text{pure 1}} (1 - x_2')\gamma_1' \tag{8-13.11}$$

where x_2' is the experimental solubility of hydrocarbon in water. Since $x_1' \ll 1$, activity coefficient $\gamma_1' = 1$. Since x_2' is very small, the calculations are not at all sensitive to x_2'.

For f_1'' we write

$$f_1'' = \phi_1'' x_1'' P \tag{8-13.12}$$

where ϕ_1'' is the fugacity coefficient as calculated from the equation of state applied to the hydrocarbon-rich liquid. P is the experimental system pressure, and x_1'' is the experimental solubility of water in the hydrocarbon. Since x_1'' and x_1' are very small, P is essentially the sum of the pure component vapor pressures.

For solubilities of water in hydrocarbons in the range 0 to 200°C, Tsonopoulos and Wilson obtained a good correlation with temperature-independent values of k_{12} (0.260 for water in benzene, 0.519 in cyclohexane, and 0.486 in n-hexane).

Although Eq. (8-13.10) is the equilibrium condition for water, a similar equation can be written for the hydrocarbon; solubility data for the hydrocarbon in water can then be used to obtain k_{12} or, alternatively, the k_{12} values obtained from solubility data for water in the hydrocarbon can be used to predict solubilities of hydrocarbons in water. That prediction is very poor, or what is equivalent, k_{12} obtained from water-in-hydrocarbon solubility data is very much different from k_{12} obtained from hydrocarbon-in-water solubility data. In other words, for a fixed binary system at constant temperature, k_{12} depends on composition. Such dependence tells us that the quadratic mixing rule for constant a is not correct. However, since the second virial coefficient $B(x)$ of a mixture is related simply to equation-of-state constants† and, since the second virial coefficent must be a quadratic function of x, we face a dilemma: at low densities, constant a is quadratic in x, but at high densities it is not. In principle, the solution to this dilemma is provided by density-dependent mixing rules as briefly discussed earlier. While equations of state provide an attractive tool for

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†For an equation of the van der Waals form, $B(x) = b(x) - a(x)/RT$.

describing liquid-liquid equilibria, most published studies are limited to binary systems.

8-14 Phase Equilibria in Polymer Solutions

Strong negative deviations from Raoult's law are observed in binary liquid mixtures where one component consists of very large molecules (polymers) and the other consists of molecules of normal size. For mixtures of normal solvents and amorphous polymers, phase equilibrium relations are usually described by the Flory-Huggins theory, discussed fully in a book by Flory [34] and in a monograph by Tompa [121]; a brief introduction is given by Prausnitz et al. [97]. For engineering application, a useful summary is provided by Sheehan and Bisio [112].

There are several versions of the Flory-Huggins theory, and unfortunately, different authors use different notation. The primary composition variable for the liquid phase is the volume fraction, here designated by Φ and defined by Eqs. (8-10.3) and (8-10.4). In polymer-solvent systems, volume fractions are very different from mole fractions because the molar volume of a polymer is much larger than that of the solvent.

Since the molecular weight of the polymer is often not known accurately, it is difficult to determine the mole fraction. Therefore, an equivalent definition of Φ is frequently useful:

$$\Phi_1 = \frac{w_1/\rho_1}{w_1/\rho_1 + w_2/\rho_2} \quad \text{and} \quad \Phi_2 = \frac{w_2/\rho_2}{w_1/\rho_1 + w_2/\rho_2} \tag{8-14.1}$$

where w_i is the weight fraction of component i and ρ_i is the mass density (*not* molar density) of pure component i.

Let subscript 1 stand for solvent and subscript 2 for polymer. The activity a_1 of the solvent, as given by the Flory-Huggins equation, is

$$\ln a_1 = \ln \Phi_1 + \left(1 - \frac{1}{m}\right)\Phi_2 + \chi\Phi_2^2 \tag{8-14.2}$$

where m is defined by $m = V_2^l/V_1^l$ and the adjustable constant χ is called the *Flory interaction parameter*. In typical polymer solutions $1/m$ is negligibly small compared with unity, and therefore it may be neglected. The parameter χ depends on temperature, but for polymer-solvent systems in which the molecular weight of the polymer is very large, it is nearly independent of polymer molecular weight. In theory, χ is also independent of polymer concentration, but in fact it often varies with concentration, especially in mixtures containing polar molecules, for which the Flory-Huggins theory provides only a rough approximation.

In a binary mixture of polymer and solvent at ordinary pressures, only the solvent is volatile; the vapor phase mole fraction of the solvent is

unity, and therefore the total pressure is equal to the partial pressure of the solvent.

In a polymer solution, the activity of the solvent is given by

$$a_1 = \frac{P}{P_{vp1}} \frac{1}{\mathcal{F}_1} \tag{8-14.3}$$

where factor $\mathcal{F}_1$ is defined by Eq. (8-4.2). At low or moderate pressures, $\mathcal{F}_1$ is equal to unity.

Equation (8-14.2) holds only for temperatures at which the polymer in the pure state is amorphous. If the pure polymer has appreciable crystallinity, corrections to Eq. (8-14.2) are significant, as discussed elsewhere [34].

Equation (8-14.2) is useful for calculating the volatility of a solvent in a polymer solution, provided that the Flory parameter χ is known. Sheehan and Bisio [112] report Flory parameters for a large number of binary systems† and present methods for estimating χ from solubility parameters. Similar data are also given in the *Polymer Handbook* [9]. Table 8-32 shows some χ values reported by Sheehan and Bisio.

A particularly convenient and rapid experimental method for obtaining χ is provided by gas-liquid chromatography [44]. Although this experimental technique can be used at finite concentrations of solvent, it is most efficiently used for solutions infinitely dilute with respect to solvent, i.e., at the limit where the volume fraction of polymer approaches unity. Some

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†Unfortunately, Sheehan and Bisio use completely different notation; v for Φ, x for m, and μ for χ.

TABLE 8-32 Flory χ Parameters for Some Polymer-Solvent Systems near Room Temperature [112]

Polymer	Solvent	χ
Natural rubber	Heptane	0.44
	Toluene	0.39
	Ethyl acetate	0.75
Polydimethyl siloxane	Cyclohexane	0.44
	Nitrobenzene	2.2
Polyisobutylene	Hexadecane	0.47
	Cyclohexane	0.39
	Toluene	0.49
Polystyrene	Benzene	0.22
	Cyclohexane	0.52
Polyvinyl acetate	Acetone	0.37
	Dioxane	0.41
	Propanol	1.2

solvent volatility data obtained from chromatography [84] are shown in Fig. 8-23. From these data, χ can be found by rewriting Eq. (8-14.2) in terms of a weight fraction activity coefficient Ω

$$\Omega_1 \equiv \frac{a_1}{w_1} = \frac{P}{P_{vp1} w_1} \frac{1}{\mathcal{F}_1} \tag{8-14.4}$$

Combining with Eq. (8-14.2), in the limit as $\Phi_2 \to 1$, we obtain

$$\chi = \ln \left(\frac{P}{w} \right)_1^\infty - \left(\ln P_{vp1} + \ln \frac{\rho_2}{\rho_1} + 1 \right) \tag{8-14.5}$$

where ρ is the mass density (*not* molar density). Equation (8-14.5) also assumes that $\mathcal{F}_1 = 1$ and that $1/m \ll 1$. Superscript ∞ denotes that weight fraction w_1 is very small compared with unity. Equation (8-14.5) provides a useful method for finding χ because $(P/w)_1^\infty$ is easily measured by gas-liquid chromatography.

Equation (8-14.2) was derived for a binary system, i.e., one in which all polymer molecules have the same molecular weight (monodisperse system). For mixtures containing one solvent and one polymer with a variety
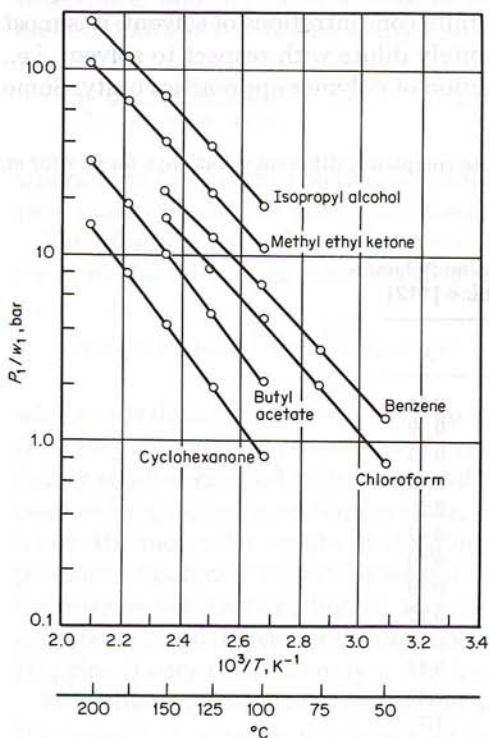

Figure 8-23 Volatilities of solvents in Lucite 2044 for a small weight fraction of solute. (*From Ref. 84.*)

of molecular weights (polydisperse system), Eq. (8-14.2) can be used provided m and Φ refer to the polymer whose molecular weight is the number average molecular weight.

The theory of Flory and Huggins can be extended to multicomponent mixtures containing any number of polymers and any number of solvents. No ternary (or higher) constants are required.

Solubility relations (liquid-liquid equilibria) can also be calculated with the Flory-Huggins theory. Limited solubility is often observed in solvent-polymer systems, and it is common in polymer-polymer systems (incompatibility). The Flory-Huggins theory indicates that, for a solvent-polymer system, limited miscibility occurs when

$$\chi > \frac{1}{2}\left(1 + \frac{1}{m^{1/2}}\right)^2 \tag{8-14.6}$$

For large m, the value of χ may not exceed $\frac{1}{2}$ for miscibility in all proportions.

Liquid-liquid phase equilibria in polymer-containing systems are described in numerous articles published in journals devoted to polymer science and engineering. The thermodynamics of such equilibria is discussed in Flory's book and in articles by Scott and Tompa [110] and by Hsu and Prausnitz [57]. A comprehensive review of polymer compatibility and incompatibility is given by Krause [63].

For semiquantitative calculations the three-dimensional solubility parameter concept [47] is often useful, especially for formulations of paints, coating, inks, etc.

The Flory-Huggins equation contains only one adjustable binary parameter. For simple nonpolar systems one parameter is often sufficient, but for complex systems, much better representation is obtained by empirical extension of the Flory-Huggins theory using at least two adjustable parameters, as shown by Maron and Nakajima [72] and by Heil and Prausnitz [53]. The latters' extension is a generalization of Wilson's equation. The UNIQUAC equation with two adjustable parameters is also applicable to polymer solutions [4].

The theory of Flory and Huggins is based on a lattice model which ignores free-volume differences; in general, polymer molecules in the pure state pack more densely than molecules of normal liquids. Therefore, when polymer molecules are mixed with molecules of normal size, the polymer molecules gain freedom to exercise their rotational and vibrational motions; at the same time, the smaller solvent molecules partially lose such freedom. To account for these effects, an *equation-of-state theory* of polymer solutions has been developed by Flory [35] and Patterson [89] based on ideas suggested by Prigogine [102]. The newer theory is necessarily more complicated, but, unlike the older one, it can at least

semiquantitatively describe some forms of phase behavior commonly observed in polymer solutions. In particular, it can explain the observation that some polymer-solvent systems exhibit lower consolute temperatures as well as upper consolute temperatures (Fig. 8-19).† Engineering applications of the theory are indicated by Bonner [17], Bondi [16], and Tapavicza [117]. Application to phase equilibria in the system polyethylene-ethylene at high pressures is discussed by Liu and Prausnitz [69].

8-15 Solubilities of Solids in Liquids

The solubility of a solid in a liquid is determined not only by the intermolecular forces between solute and solvent but also by the melting point and the enthalpy of fusion of the solute. For example, at 25°C, the solid aromatic hydrocarbon phenanthrene is highly soluble in benzene; its solubility is 20.7 mole percent. By contrast, the solid aromatic hydrocarbon anthracene, an isomer of phenanthrene, is only slightly soluble in benzene at 25°C; its solubility is 0.81 mole percent. For both solutes, intermolecular forces between solute and benzene are essentially identical. However, the melting points of the solutes are significantly different: phenanthrene melts at 100°C and anthracene at 217°C. In general, it can be shown that, when other factors are held constant, the solute with the higher melting point has the lower solubility. Also, when other factors are held constant, the solute with the higher enthalpy of fusion has the lower solubility.

These qualitative conclusions follow from a quantitative thermodynamic analysis given in several texts. (See, for example, Refs. 54 and 97.)

In a binary system, let subscript 1 stand for solvent and subscript 2 for solute. Assume that the solid phase is pure. At temperature T, the solubility (mole fraction) x_2 is given by

$$\ln \gamma_2 x_2 = -\frac{\Delta h_f}{RT}\left(1 - \frac{T}{T_t}\right) + \frac{\Delta C_p}{R}\left(\frac{T_t - T}{T}\right) - \frac{\Delta C_p}{R}\ln\frac{T_t}{T} \qquad (8\text{-}15.1)$$

where Δh_f is the enthalpy of fusion of the solute at the triple-point temperature T_t and ΔC_p is given by the molar heat capacity of the pure solute:

$$\Delta C_p = C_p \text{ (subcooled liquid solute)} - C_p \text{ (solid solute)} \qquad (8\text{-}15.2)$$

The standard state for activity coefficient γ_2 is pure (subcooled) liquid 2 at system temperature T.

To a good approximation, we can substitute normal melting temperature T_m for triple-point temperature T_t, and we can assume that Δh_f is essentially the same at the two temperatures. In Eq. (8-15.1) the first term

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†However, in polymer-solvent systems, the upper consolute temperature usually is below the lower consolute temperature.

on the right-hand side is much more important than the remaining two terms, and therefore a simplified form of that equation is

$$\ln \gamma_2 x_2 = -\frac{\Delta h_f}{RT}\left(1 - \frac{T}{T_m}\right) \qquad (8\text{-}15.3)$$

If we substitute

$$\Delta s_f = \frac{\Delta h_f}{T_m} \qquad (8\text{-}15.4)$$

we obtain an alternative simplified form

$$\ln \gamma_2 x_2 = -\frac{\Delta s_f}{R}\left(\frac{T_m}{T} - 1\right) \qquad (8\text{-}15.5)$$

where Δs_f is the entropy of fusion. A plot of Eq. (8-15.5) is shown in Fig. 8-24.

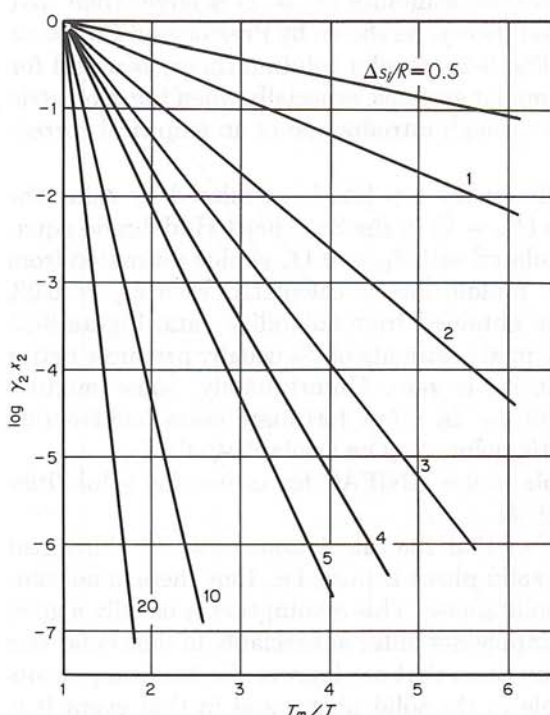If we let $\gamma_2 = 1$, we can readily calculate the ideal solubility at temper-

Figure 8-24 Activities of solid solutes referred to their pure subcooled liquids. *(From Ref. 101.)*

ature T, knowing only the solute's melting temperature and its enthalpy (or entropy) of fusion. This ideal solubility depends only on properties of the solute; it is independent of the solvent's properties. The effect of intermolecular forces between molten solute and solvent are reflected in the activity coefficient γ_2.

To describe γ_2, we can utilize any of the expressions for the excess Gibbs energy, as discussed in Sec. 8-5. However, since γ_2 depends on the mole fraction x_2, solution of Eq. (8-15.5) requires iteration. For example, suppose that γ_2 is given by a simple one-parameter Margules equation

$$\ln \gamma_2 = \frac{A}{RT} (1 - x_2)^2 \tag{8-15.6}$$

where A is an empirical constant. Substitution into Eq. (8-15.5) gives

$$\ln x_2 + \frac{A}{RT} (1 - x_2)^2 = -\frac{\Delta s_f}{R} \left(\frac{T_m}{T} - 1 \right) \tag{8-15.7}$$

and x_2 must be found by a trial-and-error calculation.

In nonpolar systems, the activity coefficient γ_2 can often be estimated by using the Scatchard-Hildebrand equation, as discussed in Sec. 8-10. In that event, since $\gamma_2 \geqslant 1$, the ideal solubility ($\gamma_2 = 1$) is larger than that obtained from regular solution theory. As shown by Preston and Prausnitz [101], and as illustrated in Fig. 8-25, regular solution theory is useful for calculating solubilities in nonpolar systems, especially when the geometric mean assumption is relaxed through introduction of an empirical correction ℓ_{12} (see Sec. 8-10).

Figure 8-25 shows three lines: the top line is calculated by using the geometric mean assumption ($\ell_{12} = 0$) in the Scatchard-Hildebrand equation. The bottom line is calculated with $\ell_{12} = 0.11$, a value estimated from gas-phase PVTy data. The middle line is calculated with $\ell_{12} = 0.08$, which is the optimum value obtained from solubility data. Figure 8-25 suggests that even an approximate estimate of ℓ_{12} usually produces better results than assuming that ℓ_{12} is zero. Unfortunately, *some* mixture datum is needed to estimate ℓ_{12}. In a few fortunate cases one freezing point datum, e.g., the eutectic point, may be available to fix ℓ_{12}.

In some cases it is possible to use UNIFAC for estimating solubilities of solids, as discussed in Ref. 41.

It is important to remember that the calculations outlined above rest on the assumption that the solid phase is pure, i.e., that there is no solubility of the solvent in the solid phase. This assumption is usually a good one, especially if the two components differ appreciably in molecular size and shape. However, in many cases that are known, the two components are at least partially miscible in the solid phase, and in that event it is necessary to correct for solubility and nonideality in the solid phase as

well as in the liquid phase. This complicates the thermodynamic treatment, but, more important, solubility in the solid phase may significantly affect the phase diagram. Figure 8-26 shows results for the solubility of solid argon in liquid nitrogen. The top line presents calculated results assuming that x^s (argon) $= 1$, where superscript ^{s} denotes the solid phase. The bottom line takes into account the experimentally known solubility of nitrogren in solid argon [x^s (argon) $\neq 1$]. In this case is it clear that serious error is introduced by neglecting solubility of the solvent in the solid phase.

8-16   Aqueous Solutions of Electrolytes

Physical chemists have given much attention to aqueous mixtures containing solutes that ionize either completely (e.g., strong salts like sodium chloride) or partially (e.g., sulfur dioxide and acetic acid). The thermodynamics of such mixtures is discussed in numerous references, but the
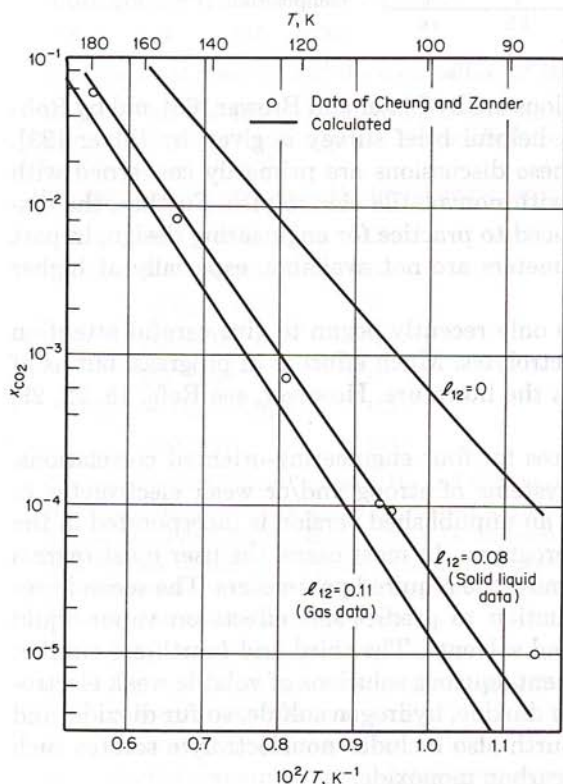
Figure 8-25 Solubility of carbon dioxide in propane. *(From Ref. 101.)*
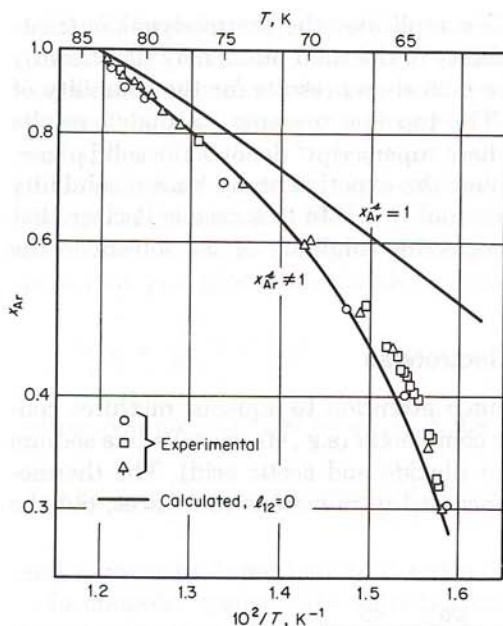
Figure 8-26 Solubility of argon in nitrogen: effect of solid-phase composition. *(From Ref. 101.)*

most useful general discussions are by Pitzer and Brewer [68] and by Robinson and Stokes [107]. A helpful brief survey is given by Pitzer [93]. Unfortunately, however, these discussions are primarily concerned with single-solute systems and with nonvolatile electrolytes. Further, the discussions are not easily reduced to practice for engineering design, in part because the required parameters are not available, especially at higher temperatures.

Chemical engineers have only recently begun to give careful attention to aqueous mixtures of electrolytes. Much effort is in progress, but as of 1984, little has appeared in the literature. However, see Refs. 18, 22, 29, 46, 75, and 94.

Table 8-33 gives references for four engineering-oriented correlations. The first is designed for systems of strong and/or weak electrolytes in aqueous or mixed solvents; an unpublished version is incorporated in the ASPEN PLUS computer programs. In most cases, the user must regress experimental data to determine the required parameters. The second uses a modified UNIQUAC equation to predict salt effects on vapor-liquid equilibria in simple or mixed solvents. The third and fourth are similar; both focus on multicomponent aqueous solutions of volatile weak electrolytes (e.g., ammonia, carbon dioxide, hydrogen sulfide, sulfur dioxide, and hydrogen cyanide). The fourth also includes nonelectrolyte solutes such as methane, nitrogen, and carbon monoxide.

A monograph edited by Furter [40] discusses salt effects on vapor-liquid equilibria in solvent mixtures.

TABLE 8-33   Four Engineering-Oriented Correlations for Vapor-Liquid Equilibria for Aqueous Solutions of Electrolytes

1. C. C. Chen, H. I. Britt, J. F. Boston, and L. B. Evans: *AIChE J.*, **28:** 533 (1982); B. Mock, L. B. Evans, and C. C. Chen: *Proc. 1984 Summer Computer Simulation Conf.*, (1984) p. 558; C. C. Chen, J. F. Boston, and L. B. Evans; also B. Mock, C. C. Chen, and L. B. Evans: papers presented at *AIChE Annual Meeting, San Francisco, November 1984.*

2. B. Sander, A. Fredenslund, and P. Rasmussen: paper presented at *AIChE Annual Meeting, San Francisco, November 1984.*

3. D. Beutier, and H. Renon: *IEC Proc. Des. Dev.*, **17:** 220 (1978): corrections, *ibid.* **19:** 722 (1980). Updated in *Thermodynamics of Aqueous Systems with Industrial Applications, ACS Symposium Series 133,* edited by S. A. Newman, 1980, p. 173.

4. T. J. Edwards, G. Maurer, J. Newman, and J. M. Prausnitz: *AIChE J.*, **24:** 966 (1978).

Example 8-17   Vapor-liquid equilibria are required for design of a sour water stripper. An aqueous stream at 120°C has the following composition, expressed in molality (moles per kilogram of water):

CO_2	0.4	NH_3	2.62	CO	0.0016
H_2S	1.22	CH_4	0.003		

Find the total pressure and the composition of the equilibrium vapor phase.

solution   This is a bubble point problem with three volatile weak electrolytes and two nonreacting ("inert") gases. The method for solution follows that outlined by Edwards et al. [32].

For the chemical species in the liquid phase, we consider the following equilibria:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ \qquad + OH^- \qquad (8\text{-}16.1)$$

$$CO_2 + H_2O \rightleftharpoons HCO_3^- \qquad + H^+ \qquad (8\text{-}16.2)$$

$$HCO_3^- \rightleftharpoons CO_3^{2-} \qquad + H^+ \qquad (8\text{-}16.3)$$

$$H_2S \rightleftharpoons HS^- \qquad + H^+ \qquad (8\text{-}16.4)$$

$$HS^- \rightleftharpoons S^{2-} \qquad + H^+ \qquad (8\text{-}16.5)$$

$$NH_3 + HCO_3^- \rightleftharpoons NH_2COO^- + H_2O \qquad (8.16.6)$$

$$H_2O \rightleftharpoons H^+ \qquad + OH^- \qquad (8.16.7)$$

We assume that "inert" gases CH_4 and CO do not participate in any reactions and that their fugacities are proportional to their molalities (Henry's law).

As indicated by Eqs. (8-16.1) to (8-16.7), we must find the concentrations of thirteen species in the liquid phase (not counting water) and six in the vapor phase (the three volatile weak electrolytes, the two inert gases, and water).

We have the following unknowns:

m_i molality of noninert chemical species i in solution (11 molalities)

γ_i^* activity coefficient of noninert chemical species i in solution (molality scale, unsymmetric convention) (11 activity coefficients)

a_w activity of liquid water (one activity)

p_i partial pressure of each volatile component i (six partial pressures)

ϕ_i fugacity coefficient of volatile component i in the vapor (six fugacity coefficients)

We have 35 unknowns; we must now find 35 independent relations among these variables.

REACTION EQUILIBRIA. The equilibrium constant is known for each of the seven reactions at 120°C. For any reaction of the form

$$A \to B^+ + C^-$$
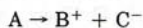
the equilibrium constant K is given by

$$K = \frac{a_{B^+} a_{C^-}}{a_A} = \frac{\gamma_B^* \gamma_C^* + m_{B^+} m_{C^-}}{a_A} \tag{8-16.8}$$

where a = activity.

ACTIVITY COEFFICIENTS. Activity coefficients for the (noninert) chemical species in solution are calculated from an expression based on the theory of Pitzer [92] as a function of temperature and composition. Binary interaction parameters are given by Edwards et al. [32]

WATER ACTIVITY. By applying the Gibbs-Duhem equation to expressions for the solute activity coefficients, we obtain an expression for the activity of liquid water as a function of temperature and composition. (See Edwards et al. [32]).

VAPOR-LIQUID EQUILIBRIA. For each volatile weak electrolyte and for each "inert" gas, we equate fugacities in the two phases:

$$\phi_i p_i = m_i \gamma_i^* H_i \text{ (PC)} \tag{8-16.9}$$

where H_i is Henry's constant for volatile solute i. For the "inert" gases in liquid solution, m_i is given and γ_i^* is taken as unity. PC is the Poynting correction. For water, the equation for phase equilibrium is:

$$\phi_w p_w = a_w P_w^{sat} \phi_w^{sat} \text{ (PC)} \tag{8-16.10}$$

where the superscripts refer to pure, saturated liquid.

Henry's constants are available at 120°C. For the Poynting correction, liquid-phase partial molar volumes are estimated.

VAPOR PHASE FUGACITY COEFFICIENTS. Since some of the components in the gas phase are polar and the total pressure is likely to exceed 1 bar, it is necessary to correct for vapor phase nonideality. The method of Nakamura et al. [83] is used to calculate fugacity coefficients as a function of temperature, pressure, and composition.

MATERIAL BALANCES A material balance is written for each weak electrolyte in the liquid phase. For example, for NH_3:

$$m_{NH_3}^o = m_{NH_3} + m_{NH_4^+} + m_{NH_2COO^-} \tag{8-16.11}$$

where m^o is the nominal concentration of the solute as specified in the problem statement.

ELECTRONEUTRALITY. Since charge is conserved, the condition for electroneutrality is given by

$$\sum_i z_i m_i = 0 \tag{8-16.12}$$

where z_i is the charge on chemical species i.

TOTAL NUMBER OF INDEPENDENT RELATIONS. We have seven reaction equilibria, eleven activity coefficient expressions, one equation for the water activity, six vapor-liquid equilibrium relations, six equations for vapor phase fugacities, three material balances, and one electroneutrality condition, providing a total of 35 independent equations.

TABLE 8-34   Program Tides Results

Input specifications: Temperature = 393.15 K
component   stoichiometric concentration

CO_2	0.40000
H_2S	1.2200
NH_3	2.6200
CH_4	0.003
CO	0.0016

	Liquid phase		Vapor phase		
Component	Concentration, molality	Activity coef., unitless	Partial pressure, atm.	Fug. coef.	Poynt. corr.
NH_3	0.97193	1.0147	0.41741	0.95997	0.98420
NH_4^+	1.4873	0.52287			
CO_2	0.27749×10^{-1}	1.0925	3.9433	0.97193	0.98219
HCO_3^-	0.20513	0.57394			
CO_3^{2-}	0.63242×10^{-2}	0.15526×10^{-1}			
H_2S	0.11134	1.1784	4.4096	0.95444	0.98092
HS^-	1.1086	0.56771			
S^{2-}	0.11315×10^{-4}	0.14992×10^{-1}			
NH_2COO^-	0.16080	0.42682			
H^+	0.83354×10^{-7}	0.86926			
OH^-	0.23409×10^{-4}	0.59587			
CH_4	0.30000×10^{-2}		3.3627	0.99758	0.97975
CO	0.16000×10^{-2}		2.0580	1.0082	0.98053
				H_2O vap. press.	1.9596 atm.
	Activity H_2O	0.93393			
		Total pressure	16.154 atm.		

Equilibrium constants at 393.15 K

Reaction	Equil. constant	units
NH_3 dissociation	0.11777×10^{-4}	molality
CO_2 dissociation	0.30127×10^{-6}	molality
HCO_3 dissociation	0.60438×10^{-10}	molality
H_2S dissociation	0.34755×10^{-6}	molality
HS dissociation	0.19532×10^{-13}	molality
NH_2CO formation	0.55208	1/molality
H_2O dissociation	0.10821×10^{-11}	molality^2

Henry's constants, $kg \cdot atm/mol$

CO_2	124.52
H_2S	31.655
NH_3	0.40159
CH_4	1091.3
CO	1263.9

Computer program TIDES† is designed to perform the tedious trial-and-error calculations. For this bubble point problem, the only required inputs are the temperature and the molalities of the nominal (stoichiometric) solutes in the liquid phase. The total pressure is 16.4 bar, and the calculated mole fractions in the vapor phase are:

CO_2	0.243	CH_4	0.208
H_2S	0.272	CO	0.127
NH_3	0.026	H_2O	0.122

Table 8-34 shows the program output. Note that activities of solutes have units of molality. However, all activity coefficients and the activity of water are dimensionless.

8-17 Concluding Remarks

This chapter on phase equilibria has presented no more than a brief introduction to a very broad subject. The variety of mixtures encountered in the chemical industry is extremely large, and, except for general thermodynamic equations, there are no quantitative relations which apply rigorously to all, or even to a large fraction, of these mixtures. Thermodynamics provides only a coarse but reliable framework; the details must be supplied by physics and chemistry, which ultimately rest on experimental data.

For each mixture it is necessary to construct an appropriate mathematical model for representing the properties of that mixture. Whenever possible, such a model should be based on physical concepts, but since our fundamental understanding of fluids is severely limited, any useful model is inevitably influenced by empiricism. While at least some empiricism cannot be avoided, the strategy of the process engineer must be to use enlightened rather than blind empiricism. This means foremost that critical and informed judgment must always be exercised. While such judgment is attained only by experience, we conclude this chapter with a few guidelines.

1. Face the facts: you cannot get something from nothing. Do not expect magic from thermodynamics. If you want reliable results, you will need some reliable experimental data. You may not need many, but you do need some. The required data need not necessarily be for the particular system of interest; sometimes they may come from experimental studies on closely related systems, perhaps represented by a suitable correlation. Only in very simple cases can partial thermodynamic properties in a mixture, e.g., activity coefficients, be found from pure-component data alone.

2. Correlations provide the easy route, but they should be used last, not

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†Available from J. M. Prausnitz, Department of Chemical Engineering, University of California, Berkeley.

first. The preferred first step should always be to obtain *reliable* experimental data, either from the literature or from the laboratory. Do not at once reject the possibility of obtaining a few crucial data yourself. Laboratory work is more tedious than pushing a computer button, but ultimately, at least in some cases, you may save time by making a few simple measurements instead of a multitude of furious calculations. A small laboratory with a few analytical instruments (especially a chromatograph or a simple boiling-point apparatus) can often save both time and money. If you cannot do the experiment yourself, consider the possibility of having someone else do it for you.

3. It is always better to obtain a few well-chosen and reliable experimental data than to obtain many data of doubtful quality and relevance. Beware of statistics, which may be the last refuge of a poor experimentalist.

4. Always regard published experimental data with skepticism. Many experimental results are of high quality, but many are not. Just because a number is reported by someone and printed by another, do not automatically assume that it must therefore be correct.

5. When choosing a mathematical model for representing mixture properties, give preference if possible to those which have some physical basis.

6. Seek simplicity; beware of models with many adjustable parameters. When such models are extrapolated even mildly into regions other than those for which the constants were determined, highly erroneous results may be obtained.

7. In reducing experimental data, keep in mind the probable experimental uncertainty of the data. Whenever possible, give more weight to those data which you have reason to believe are more reliable.

8. If you do use a correlation, be sure to note its limitations. Extrapolation outside its domain of validity can lead to large error.

9. Never be impressed by calculated results merely because they come from a computer. The virtue of a computer is speed, not intelligence.

10. Maintain perspective. Always ask yourself: Is this result reasonable? Do other similar systems behave this way? If you are inexperienced, get help from someone who has experience. Phase equilibria in fluid mixtures is not a simple subject. Do not hesitate to ask for advice.

Notation

$a, b, c,$	empirical coefficients	aa	empirical parameter in Eq. (8-10.28)
a_i	activity of component i		
a_{mn}	group interaction parameter, Eq. (8-10.57)	A	empirical constant
		B	empirical constant

B_{ij}	second virial coefficient for the ij interaction	ℓ_i	constant defined in Table 8-3
c, d	empirical constants in Eq. (8-7.1)	ℓ_{12}	empirical constant in Sec. 8-10
c_{ij}	cohesive energy density for the ij interaction in Sec. 8-10.	m	defined after Eq. (8-14.2); defined by Eq. (8-12.13)
c_{12}	empirical constant in Eq. (8-5.14).	m_i	molality in Sec. 8-16
C	empirical constant	n_i	number of moles of component i
C_p	molar specific heat at constant pressure	n_T	total number of moles
C_{ij}	binary parameter in Eq. (8-12.22)	N	number of components; parameter in Tables 8-17 and 8-18
d_{12}	Flory-Huggins combinatorial term in Eq. (8-10.27)	p	partial pressure
D	empirical constant; number of data points, Eq. (8-8.16)	P	total pressure
		P_{vp}	vapor pressure
D_{ij}	binary parameter in Eq. (8-12.23)	POL	defined by Eq. (8-10.33)
f_i	fugacity of component i	q	molecular surface parameter, an empirical constant (Table 8-3); induction parameter in Eq. (8-10.27)
f	a function		
$\mathcal{F}_i$	nonideality factor defined by Eq. (8-4.2)	Q_k	group surface parameter, Eq. (8-10.53)
g_{ij}	empirical constant (Table 8-3)	r	molecular-size parameter, an empirical constant (Table 8-3); number of rings (Table 8-18)
g^E	molar excess Gibbs energy		
G^E	total excess Gibbs energy	R	gas constant
G_{ij}	empirical constant (Table 8-3)	R_k	group size parameter, Eq. (8-10.53)
h^E	molar excess enthalpy	$\mathcal{R}$	defined by Eq. (8-10.45)
Δh_f	molar enthalpy of fusion	RI	index of refraction (Table 8-19); also known as n_D in Eqs. (8-10.35 and 8-10.36)
$\bar{h}_i$	partial molar enthalpy of component i		
H	Henry's constant		
ΔH_v	enthalpy of vaporization	s^E	molar excess entropy
I	defined by Eq. (8-8.17)	Δs_f	molar entropy of fusion
ID	index (Table 8-19)	s_j	number of size groups in molecule j, Eq. (8-10.45)
k_{12}	binary parameter in Sec. 8-13	t	temperature
K	y/x in Sec. 8-12; distribution coefficient in Sec. 8-13; chemical equilibrium constant in Sec. 8-16	T	absolute temperature
		T_m	melting point temperature
		T_t	triple-point temperature

u_{ij}	empirical constant (Table 8-3)	η	empirical constant (Table 8-14) and Eq. (8-9.23); empirical constant in Tables 8-17 and 8-18
ΔU	change in internal energy		
V	molar volume	θ	parameter in Tables 8-17 and 8-18
V_T	total volume		
w_k	weight fraction of component k	Θ_i	surface fraction of component i (Table 8-3)
x_i	liquid phase mole fraction of component i	λ	nonpolar solubility parameter or dispersion parameter in Sec. 8-10
X_k	group mole fraction for group k	λ_{ij}	empirical constant in Eq. (8-5.11) and Table 8-14
y_i	vapor phase mole fraction of component i	Λ_{ij}	empirical constant (Table 8-3)
z	coordination number (Table 8-3); compressibility factor in Sec. 8-12	$\nu_k^{(i)}$	number of groups of type k in molecule i
z_i	overall mole fraction in Sec. 8-12; charge on chemical species i in Eq. (8-16.12)	ν_{kj}	number of interaction groups k in molecule j [Eq. (8-10.46)]
Z	compressibility factor	ξ	hydrogen-bonding asymmetry parameter in Eq. (8-10.27)
		ρ	density
GREEK		σ^2	variance, Eqs. (8-8.16) and (8-8.17)
α	parameter in Tables 8-17 and 8-18; acidity parameter in Eq. (8-10.27)	τ	polar solubility or polar parameter in Eqs. (8-10.17) and (8.10.18)
α_{ij}	empirical constant	τ_{ij}	empirical constant (Table 8-3)
β	proportionality factor in Eq. (8-5.12); basicity parameter in Eq. (8-10.27)	ϕ_i	fugacity coefficient of component i
γ_i	activity coefficient of component i	Φ_i	site fraction (or volume fraction) of component i
	activity coefficient of group k in Eq. (8-10.47)	χ	Flory interaction parameter
δ	solubility parameter defined by Eq. (8-10.10); also parameter in Eqs. (8-12.25) and (8-12.30)	Ψ_{mn}	group interaction parameter, Eq. (8-10.57)
		ψ	polarity asymmetry parameter in Eq. (8-10.27)
$\bar{\delta}$	average solubility parameter defined by Eq. (8-10.15)	ψ_{12}	binary (induction) parameter in Eq. (8-10.19)
ϵ	parameter in Tables 8-17 and 8-18	ω	acentric factor
ζ	parameter in Tables 8-17 and 8-18	Ω	coefficient in Eq. (8-12.21); weight fraction activity coefficient in Eq. (8-14.4)

SUPERSCRIPTS

c	consolute (Sec. 8-13); calculated quantity, Eqs. (8-18.15) and (8.12.17)	$^{\circ}$	standard state as in f_i°
		R	residual
C	configurational	$\mathscr{S}$	solid phase
e	experimental, Eq. (8-12.17)	s	saturation
E	excess	S	size (Sec. 8-10)
G	group (Sec. 8-10)	V	vapor phase
L	liquid phase	0	estimated true value, Eq. (8-8.16)
M	measured value, Eq. (8-8.16)	∞	infinite dilution

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Chapter

9

Viscosity

9-1 Scope

The first part of this chapter deals with the viscosity of gases and the second with the viscosity of liquids. In each part, methods are recommended for (1) correlating viscosities with temperature, (2) estimating viscosities when no experimental data are available, (3) estimating the effect of pressure on viscosity, and (4) estimating the viscosities of mixtures. The molecular theory of viscosity is considered briefly.

9-2 Definition and Units of Viscosity

If a shearing stress is applied to any portion of a confined fluid, the fluid will move and a velocity gradient will be set up within it with a maximum velocity at the point where the stress is applied. If the shear stress per unit area at any point is divided by the velocity gradient, the ratio obtained is defined as the viscosity of the medium. It can be seen, therefore, that viscosity is a measure of the internal fluid friction, which tends to oppose any dynamic change in the fluid motion; i.e., if the friction between layers of fluid is small (low viscosity), an applied shearing force will result in a large velocity gradient. As the viscosity increases, each fluid layer exerts a larger frictional drag on adjacent layers and the velocity gradient decreases.

It is to be noted that viscosity differs in one important respect from the properties discussed previously in this book; namely, viscosity is a non-equilibrium property on a macroscale. Density, for example, is an equilibrium property. On a microscale, both properties reflect the effect of molecular motion and interaction. Even though viscosity is ordinarily referred to as a nonequilibrium property, it is, like temperature, pressure, and volume, a function of the state of the fluid, and it may be used to define the state of the material.† Brulé and Starling [30] have emphasized the desirability of using both viscosity and thermodynamic data to characterize complex fluids and to develop correlations.

The mechanism or theory of gas viscosity has been reasonably well clarified by the application of the kinetic theory of gases, but the theory of liquid viscosity is poorly developed. Brief summaries of both theories will be presented.

Since viscosity is defined as a shearing stress per unit area divided by a velocity gradient, it should have the dimensions of (force)(time)/(length)^2 or mass/(length)(time). Both dimensional groups are used, although for most scientific work, viscosities are expressed in poises, centipoises, micropoises, etc. A poise (P) denotes a viscosity of 0.1 N·s/m^2 and 1.0 cP = 0.01 P. The following conversion factors apply to the viscosity units:

$$1 \text{ P} = 1.000 \times 10^2 \text{ cP} = 1.000 \times 10^6 \text{ } \mu\text{P} = 0.1 \text{ N s/m}^2$$
$$= 6.72 \times 10^{-2} \text{ lb-mass/(ft·s)} = 242 \text{ lb-mass/(ft·h)}$$

The *kinematic viscosity* is the ratio of the viscosity to the density. With viscosity in poises and the density of grams per cubic centimeter, the unit of kinematic viscosity is the *stoke,* with the units square centimeters per second. In the SI system of units, viscosities are expressed in N·s/m^2 (or Pa·s) and kinematic viscosities in either m^2/s or cm^2/s.

9-3 Theory of Gas Transport Properties

The theory of gas transport properties is simply stated, but it is quite complex to express in equations which can be used directly to calculate viscosities. In simple terms, when a gas undergoes a shearing stress so that there is some bulk motion, the molecules at any one point have the bulk velocity vector added to their own random velocity vector. Molecular collisions cause an interchange of momentum throughout the fluid, and this bulk motion velocity (or momentum) becomes distributed. Near the source of the applied stress, the bulk velocity vector is high, but as the

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†This discussion is limited to Newtonian fluids, i.e., fluids in which the viscosity, as defined, is independent of either the magnitude of the shearing stress or velocity gradient (rate of shear).

molecules move away from the source, they are "slowed down" (in the direction of bulk flow), which causes the other sections of the fluid to move in that direction. This random, molecular momentum interchange is the predominant cause of gaseous viscosity.

Elementary kinetic theory

If the gas is modeled in the simplest manner, it is possible to show the general relations among viscosity, temperature, pressure, and molecular size. More rigorous treatments will yield similar relations which contain important correction factors. The elementary gas model assumes all molecules to be noninteracting rigid spheres of diameter σ (with mass m) moving randomly at a mean velocity v. The density is n molecules in a unit volume. Molecules move in the gas and collide, and they may transfer momentum or energy if there are velocity or temperature gradients. Such processes also result in a transfer of molecular species if a concentration gradient exists. The net flux of momentum, energy, or component mass between two layers is assumed proportional to the momentum, energy, or mass density gradient, i.e.,

$$\text{Flux} \propto -\frac{d\rho'}{dz} \tag{9-3.1}$$

where the density ρ' decreases in the $+z$ direction and ρ' may be ρ_i (mass density), nmv_y (momentum density), or $C_v nT$ (energy density). The coefficient of proportionality for all these fluxes is given by elementary kinetic theory as $vL/3$, where v is the average molecular speed and L is the mean free path.

Equation (9-3.1) is also used to define the transport coefficients of diffusivity D, viscosity η, and thermal conductivity λ; that is,

$$\text{Mass flux} = -Dm\frac{dn_i}{dz} = -\frac{vL}{3}\frac{d\rho_i}{dz} \tag{9-3.2}$$

$$\text{Momentum flux} = -\eta\frac{dv_y}{dz} = -\frac{vL}{3}mn\frac{dv_y}{dz} \tag{9-3.3}$$

$$\text{Energy flux} = -\lambda\frac{dT}{dz} = -\frac{vL}{3}C_v n\frac{dT}{dz} \tag{9-3.4}$$

Equations (9-3.2) to (9-3.4) define the transport coefficients D, η, and λ. If the average speed is proportional to $(RT/M)^{1/2}$ and the mean free path to $(n\sigma^2)^{-1}$,

$$D = \frac{vL}{3} = (\text{const})\frac{T^{3/2}}{M^{1/2}P\sigma^2} \tag{9-3.5}$$

$$\eta = \frac{m\rho v L}{3} = (\text{const}) \frac{T^{1/2}M^{1/2}}{\sigma^2} \tag{9-3.6}$$

$$\lambda = \frac{v L C_v n}{3} = (\text{const}) \frac{T^{1/2}}{M^{1/2}\sigma^2} \tag{9-3.7}$$

The constant multipliers in Eqs. (9-3.5) to (9.3-7) are different in each case; the interesting fact to note from these results is the dependency of the various transfer coefficients on T, P, M, and σ. A similar treatment for rigid, noninteracting spheres having a Maxwellian velocity distribution yields the same final equations but with slightly different numerical constants.

The viscosity relation [Eq. (9-3.6)] for a rigid, noninteracting sphere model is

$$\eta = 26.69 \frac{(MT)^{1/2}}{\sigma^2} \tag{9-3.8}$$

where η = viscosity, μP
 M = molecular weight, g/mol
 T = temperature, K
 σ = hard-sphere diameter, Å

Analogous equations for λ and D are given in Chaps. 10 and 11.

Effect of intermolecular forces

If the molecules attract or repel one another by virtue of intermolecular forces, the theory of Chapman and Enskog is normally employed [40, 100]. There are four important assumptions in this development: (1) the gas is sufficiently dilute for only binary collisions to occur, (2) the motion of the molecules during a collision can be described by classical mechanics, (3) only elastic collisions occur, and (4) the intermolecular forces act only between fixed centers of the molecules; i.e., the intermolecular potential function is spherically symmetric. With these restrictions, it would appear that the resulting theory should be applicable only to low-pressure, high-temperature monatomic gases. The pressure and temperature restrictions are valid; but for lack of tractable, alternate models, it is very often applied to polyatomic gases except in the case of thermal conductivity. Then a correction for internal energy transfer and storage must be included (see Chap. 10).

The Chapman-Enskog treatment considers in detail the interactions between colliding molecules with a potential energy $\psi(r)$ included. The equations are well known, but their solution is often very difficult. Each choice of an intermolecular potential $\psi(r)$ must be solved separately. In

general terms, the solution for viscosity is written

$$\eta = \frac{(\frac{5}{16})(\pi MRT)^{1/2}}{\pi \sigma^2 \Omega_v} = \frac{(26.69)(MT)^{1/2}}{\sigma^2 \Omega_v} \tag{9-3.9}$$

which is identical to Eq. (9-3.8) except for the inclusion of the *collision integral* Ω_v. Ω_v is unity if the molecules do not attract each other. Given a potential energy of interaction $\psi(r)$, Ω_v can be calculated; results from using the Lennard-Jones potential function are illustrated in Sec. 9-4.

9-4 Estimation of Low-Pressure Gas Viscosity

Essentially all gas viscosity estimation techniques are based on either the Chapman-Enskog theory or the law of corresponding states. Both approaches are discussed below, and recommendations are presented at the end of the section.

Theoretical approach

The Chapman-Enskog viscosity equation was given as (9-3.9).† To use this relation to estimate viscosities, the collision diameter σ and the collision integral Ω_v must be found. In the derivation of Eq. (9-3.9), Ω_v is obtained as a complex function of a dimensionless temperature T^*. The functionality depends upon the intermolecular potential chosen. As shown in Fig. 9-1, let $\psi(r)$ be the potential energy of interaction between two molecules separated by distance r. At large separation distances, $\psi(r)$ is negative; the molecules attract each other.‡ At small distances, repulsion occurs. The minimum in the $\psi(r)$ versus r curve is termed the *characteristic energy* ϵ. For any potential curve, the dimensionless temperature T^* is related to ϵ by

$$T^* = \frac{kT}{\epsilon} \tag{9-4.1}$$

where k is Boltzmann's constant. Referring again to Fig. 9-1, the collision diameter σ is defined as the separation distance when $\psi(r) = 0$.

The relation between $\psi(r)$ and r is called an *intermolecular potential function*. Such a function written by using only the parameters ϵ and σ is a two-parameter potential. The Lennard-Jones 12-6 potential given in Eq. (9-4.2) is an example of this type. Many other potential functions with

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†A correction factor, which is essentially unity, was omitted in Eq. (9-3.9).

‡The negative gradient of $\psi(r)$ is the *force* of interaction.

different or additional parameters also have been proposed. The important element, however, is that one must know how $\psi(r)$ varies with r in order to obtain Ω_v in Eq. (9-3.9). The working equation for η must have as many parameters as were used to define the original $\psi(r)$ relation.

The Lennard-Jones 12-6 potential is

$$\psi(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right] \tag{9-4.2}$$

This relation is based upon rather tenuous theoretical grounds and has been widely criticized. However, it is one of the more tractable relations for $\psi(r)$; and since Ω_v is relatively insensitive to the exact form of the $\psi(r)$ relation, Eq. (9-4.2) has been extensively used.

With this potential, the collision integral has been determined by a number of investigators [13, 100, 114, 126, 127, 148]. Neufeld et al. [150] proposed an empirical equation which is convenient for computer application:

$$\Omega_v = [A(T^*)^{-B}] + C[\exp(-DT^*)] + E[\exp(-FT^*)] \tag{9-4.3}$$

where $T^* = kT/\epsilon$, $A = 1.16145$, $B = 0.14874$, $C = 0.52487$, $D = 0.77320$, $E = 2.16178$, and $F = 2.43787$. Equation (9-4.3) is applicable from $0.3 \leq T^* \leq 100$ with an average deviation of only 0.064 percent. A graph of log Ω_v as a function of log T^* is shown in Fig. 9-2.

Distance r between molecules
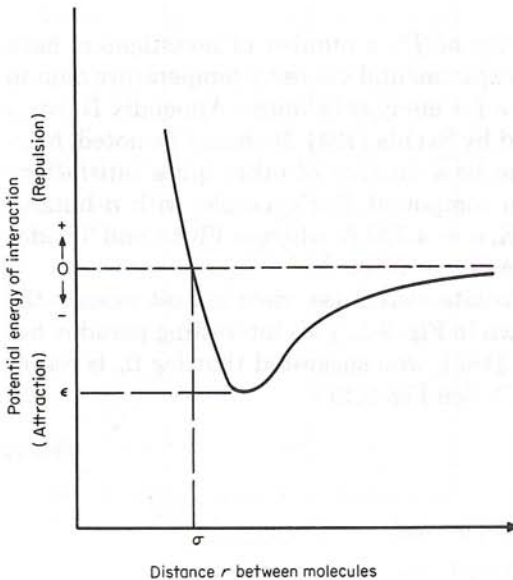
Figure 9-1 Intermolecular potential function.
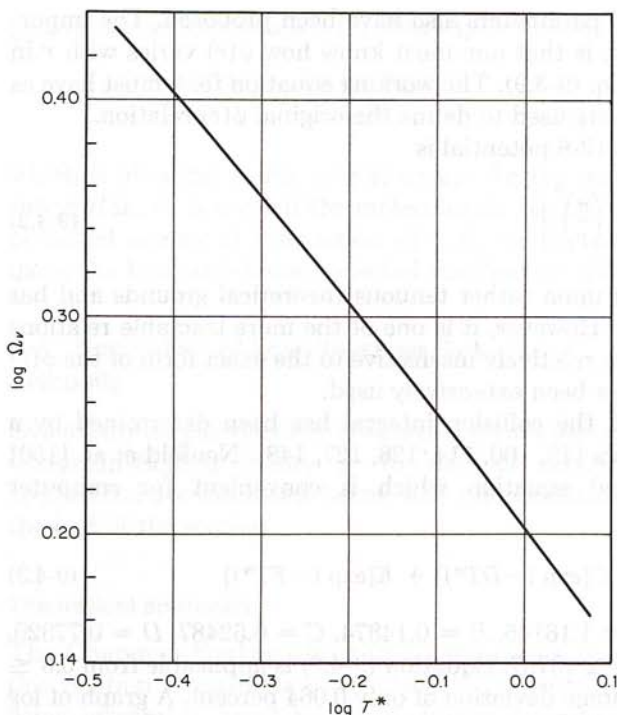
Figure 9-2 Effect of temperature on the Lennard-Jones viscosity collision integral.

With values of Ω_v as a function of T^*, a number of investigators have used Eq. (9-3.9) and regressed experimental viscosity-temperature data to find the best values of ϵ/k and σ for many substances. Appendix B lists a number of such sets as reported by Svehla [194]. It should be noted, however, that there appears also to be a number of other quite satisfactory *sets* of ϵ/k and σ for any given compound. For example, with *n*-butane, Svehla suggested $\epsilon/k = 513.4$ K, $\sigma = 4.730$ Å, whereas Flynn and Thodos [74] recommend $\epsilon/k = 208$ K and $\sigma = 5.869$ Å.

Both sets, when used to calculate viscosities, yield almost exactly the same values of viscosity as shown in Fig. 9-3. This interesting paradox has been resolved by Reichenberg [165], who suggested that $\log \Omega_v$ is essentially a linear function of $\log T^*$ (see Fig. 9-2).†

$$\Omega_v = a(T^*)^n \tag{9-4.4}$$

---

†Kim and Ross [125] do, in fact, propose that:

$\log \Omega_v = 0.2052 - 0.5 \log T^*$

where $0.4 < T^* < 1.4$. They note a maximum error of only 0.7 percent.

Equation (9-3.9) may then be written

$$\eta = 26.69 M^{1/2} T^{(0.5-n)} a^{-1} \frac{(\epsilon/k)^n}{\sigma^2} \mu P \tag{9-4.5}$$

Here the parameters σ and ϵ/k are combined as a *single* term $(\epsilon/k)^n/\sigma^2$. There is then no way of delineating individual values of ϵ/k and σ by using experimental viscosity data, at least over the range where Eq. (9-4.4) applies.

The conclusion to be drawn from this discussion is that Eq. (9-3.9) can be used to calculate gas viscosity, although the chosen set of ϵ/k and σ may have little relation to molecular properties. There will be an infinite number of acceptable sets as long as the temperature range is not too broad, e.g., if one limits the estimation to the range of reduced temperatures from about 0.3 to 1.2. In using published values of ϵ/k and σ for a fluid of interest, the two values from the same set must be used—never ϵ/k from one set and σ from another.

The difficulty in obtaining a priori meaningful values of ϵ/k and σ has led most authors to specify rules which relate ϵ/k and σ to better characterized parameters such as the critical constants. One such method is shown below.
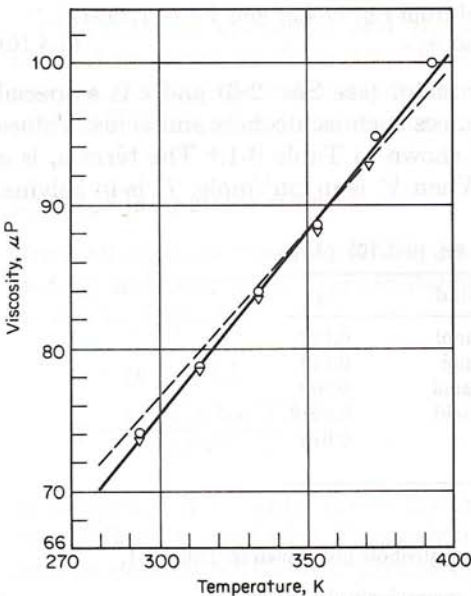
Figure 9-3 Comparison of calculated and experimental low-pressure gas viscosity of n-butane. With Eq. (9-3.9) and the Lennard-Jones Potential:

— — — Flynn and Thodos [74] with σ = 5.869 Å and ϵ/k = 208 K

———— Svehla [194] with σ = 4.730 Å and ϵ/k = 513.4 K

○ Ref. 206; ▽ Ref. 222

Method of Chung et al. [44, 45]

These authors have employed Eq. (9-3.9) with

$$\frac{\epsilon}{k} = \frac{T_c}{1.2593} \tag{9-4.6}$$

$$\sigma = 0.809 V_c^{1/3} \tag{9-4.7}$$

where ϵ/k and T_c are in kelvins, σ is in angstroms, and V_c is in cm³/mol. Then, using Eqs. (9-4.1) and (9-4.6),

$$T^* = 1.2593 T_r \tag{9-4.8}$$

Ω_v in Eq. (9-3.9) is found from Eq. (9-4.3) with T^* defined by Eq. (9-4.8). Chung et al. also multiply the right-hand side of Eq. (9-3.9) by a factor F_c to account for molecular shapes and polarities of dilute gases. Their final result may be expressed as:

$$\eta = 40.785 \frac{F_c(MT)^{1/2}}{V_c^{2/3}\Omega_v} \tag{9-4.9}$$

where η = viscosity, μP
M = molecular weight, g/mol
T = temperature, K
V_c = critical volume, cm³/mole
Ω_v = viscosity collision integral from Eq. (9-4.3) and $T^* = 1.2593 T_r$
$F_c = 1 - 0.2756\omega + 0.059035\mu_r^4 + \kappa \tag{9-4.10}$

In Eq. (9-4.10), ω is the acentric factor (see Sec. 2-3) and κ is a special correction for highly polar substances such as alcohols and acids. Values of κ for a few such materials are shown in Table 9-1.† The term μ_r is a dimensionless dipole moment.‡ When V_c is in cm³/mole, T_c is in kelvins,

TABLE 9-1   The Association Factor κ in Eq. (9-4.10) [44]

Compound	κ	Compound	κ
Methanol	0.215	n-Pentanol	0.122
Ethanol	0.175	n-Hexanol	0.114
n-Propanol	0.143	n-Heptanol	0.109
i-Propanol	0.143	Acetic Acid	0.0916
n-Butanol	0.132	Water	0.076
i-Butanol	0.132		

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†Chung et al. [45] suggest that for other alcohols not shown in Table 9-1,

$\kappa = 0.0682 + 0.2767$ [(17)(number of —OH groups)/molecular weight]

‡See the discussion under Eq. (9-4.16) for techniques to nondimensionalize a dipole moment.

and μ is in debyes,

$$\mu_r = 131.3 \frac{\mu}{(V_c T_c)^{1/2}} \tag{9-4.11}$$

Example 9-1 Estimate the viscosity of sulfur dioxide gas at atmospheric pressure and 300°C by using the Chung et al. method. The experimental viscosity is 246 μP [129].

solution From Appendix A, $T_c = 430.8$ K, $V_c = 122$ cm³/mole, $\omega = 0.256$, $M = 64.063$, and the dipole moment is 1.6 debyes. Assume κ is negligible. From Eq. (9-4.11),

$$\mu_r = \frac{(131.3)(1.6)}{[(122)(430.8)]^{1/2}} = 0.916$$

and with Eq. (9-4.10),

$$F_c = 1 - (0.2756)(0.256) + (0.059035)(0.916)^4 = 0.971$$

$$T^* = 1.2593 \frac{300 + 273}{430.8} = 1.675$$

Then, with Eq. (9-4.3), $\Omega_v = 1.256$. The viscosity is determined from Eq. (9-4.9).

$$\eta = (40.785)(0.971) \frac{[(64.063)(300 + 273)]^{1/2}}{(122)^{2/3}(1.256)} = 245.6 \ \mu P$$

$$\text{Error} = \frac{245.6 - 246}{246} \times 100 = -0.2\%$$

Experimental viscosities and those estimated by the Chung et al. method are shown in Table 9-2. The average absolute error was about 1.9 percent. This agrees well with the more extensive comparison by Chung [43], who found an average absolute error of about 1.5 percent.

Corresponding states methods

From an equation such as (9-3.9), if one associates σ^3 with V_c [as in Eq. (9-4.7)] and assumes V_c is proportional to RT_c/P_c, a dimensionless viscosity can be defined:

$$\eta_r = \xi \eta = f(T_r) \tag{9-4.12}$$

$$\xi = \left[\frac{(RT_c)(N_0)^2}{M^3 P_c^4} \right]^{1/6} \tag{9-4.13}$$

In SI units, if $R = 8314$ J/(kmol·K) and N_0 (Avogadro's number) $= 6.023 \times 10^{26}$ (kmol)$^{-1}$ and with T_c in kelvins, M in kg/kmol, and P_c in N/m², ξ has the units of m²/(N·s) or inverse viscosity. In more convenient units,

$$\xi = 0.176 \left(\frac{T_c}{M^3 P_c^4} \right)^{1/6} \tag{9-4.14}$$

Compound	T, °C	Experimental value, μP‡	Percent error†		
			Chung et al., Eq. (9-4.9)	Lucas, Eq. (9-4.15)	Reichenberg, Eq. (9-4.20)
Acetic acid	150	118	3.4	—	1.7
	250	151	0.2	—	2.4
Acetylene	30	102	0.6	0.6	2.4
	101	126	−0.6	−0.8	0.7
	200	155	−0.5	−0.6	0.7
Ammonia	37	106	2.2	2.3	—
	147	146	0.4	0.2	—
	267	189	−2.1	−1.9	—
Benzene	28	73.2	1.0	3.2	4.4
	100	92..5	0.2	1.3	2.1
	200	117	0.5	1.6	1.8
Bromotrifluoromethane	17	145	7.6	8.3	−0.3
	97	183	8.2	8.6	−0.5
Isobutane	37	79	−1.6	1.6	1.6
	155	105	2.0	4.7	4.0
	287	132	3.9	6.7	5.6
n-Butane	7	74	−5.8	−4.1	−5.6
	127	101	−1.0	0.1	−2.3
	267	132	0.6	1.5	−1.4
1-Butene	20	76.1	−1.0	1.1	1.8
	60	86.3	−0.5	1.4	1.7
	120	102	−0.6	0.9	0.9
Carbon dioxide	37	154	−0.6	1.6	—
	127	194	−0.1	2.2	—
	327	272	0.5	3.0	—
Carbon disulfide	30	100	0	5.9	—
	98.2	125	−1.3	3.5	—
	200	161	−1.9	2.2	—
Carbon tetrachloride	125	133	0.8	1.9	−2.8
	200	156	2.4	3.1	−2.1
	300	186	3.8	4.1	−1.4
Chlorine	20	133	2.2	3.5	—
	100	168	3.3	4.1	—
	200	209	4.5	5.1	—
Chloroform	20	100	−3.8	3.4	−1.0
	100	125	−1.3	5.4	0.6
	300	191	−0.9	5.1	−0.6
Cyclohexane	35	72.3	−2.4	−0.1	−4.2
	100	87.3	−1.4	0.3	−4.1
	300	129	2.6	3.6	−1.9
Dimethyl ether	20	90.9	−5.2	−1.0	2.0
	100	117	−6.1	−2.4	0.2

Compound	T, °C	Experimental value, μP‡	Percent error†		
			Chung et al., Eq. (9-4.9)	Lucas, Eq. (9-4.15)	Reichenberg, Eq. (9-4.20)
Ethane	47	100	0.1	0.7	−3.2
	117	120	0.2	0.8	−3.3
	247	156	−1.0	−0.3	−4.7
Ethyl acetate	125	101	−2.6	9.0	−1.6
	200	120	−2.4	8.8	−2.0
	300	146	−3.3	7.4	−3.5
Ethanol	110	111	−0.5	−2.5	0.6
	197	137	−0.8	1.6	−0.4
	267	156	−0.3	2.0	−0.1
Diethyl ether	125	99.1	−0.4	0.2	0.7
	200	118	−0.8	−0.5	−0.3
	300	141	−0.6	−0.4	−0.5
n-Hexane	107	81	−1.1	0.9	0.3
	267	116	−2.1	−0.7	−2.1
Methane	−13	98	−0.7	−0.5	—
	147	147	0	−0.9	—
Methyl acetate	125	108	0	10	1.7
	300	157	−1.6	7.6	−1.0
Methanol	67	112	−0.4	−0.9	1.1
	127	132	−0.3	−1.1	1.2
	277	181	−0.3	−1.7	0.9
Methyl chloride	50	119	3.9	0.8	−0.6
	130	147	5.0	1.4	1.9
Nitrogen	27	178	0.3	0.3	—
	227	258	0.3	0.4	—
Isopropanol	157	113	0.3	5.9	3.5
	257	139	0.1	5.4	2.7
Propylene	17	83	2.4	2.4	3.0
	127	115	1.5	0.9	0.8
	307	160	1.7	1.2	0.7
Sulfur dioxide	10	120	2.8	5.5	—
	100	163	0.3	2.2	—
	300	246	−0.2	1.5	—
	700	376	1.5	3.4	—
Toluene	60	78.9	−5.2	−3.7	−2.3
	250	123	−3.5	−3.1	−2.5
Average absolute error			1.9	3.0	1.9

†Percent error = [(calc. − exp.)/exp.] × 100.
‡All experimental viscosity values were obtained from Refs. 129, 137, and 188.

where ξ = reduced, inverse viscosity, $(\mu P)^{-1}$, T_c is kelvins, M is in g/mol, and P_c is in bars.

Equation (9-4.12) has been recommended by several authors [73, 83, 141, 143, 210, 225]. The specific form suggested by Lucas [135, 137, 138] is illustrated below.

$$\eta\xi = [0.807T_r^{0.618} - 0.357 \exp(-0.449T_r)$$
$$+ 0.340 \exp(-4.058T_r) + 0.018] F_P^\circ F_Q^\circ \quad (9\text{-}4.15)$$

ξ is defined by Eq. (9-4.14), η is in μP, T_r is the reduced temperature, and F_P° and F_Q° are correction factors to account for polarity or quantum effects. To obtain F_P°, a reduced dipole moment is required. Lucas defines this quantity somewhat differently than did Chung et al. in Eq. (9-4.11), i.e.,

$$\mu_r = 52.46 \frac{\mu^2 P_c}{T_c^2} \quad (9\text{-}4.16)$$

where μ is in debyes, P_c is in bars, and T_c is in kelvins.† Then F_P° values are found as:

$$F_P^\circ = 1 \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad 0 \leq \mu_r < 0.022$$
$$F_P^\circ = 1 + 30.55(0.292 - Z_c)^{1.72} \qquad\qquad\qquad 0.022 \leq \mu_r < 0.075$$
$$F_P^\circ = 1 + 30.55(0.292 - Z_c)^{1.72} \, |0.96 + 0.1(T_r - 0.7)| \quad 0.075 \leq \mu_r$$

$$(9\text{-}4.17)$$

The factor F_Q° is used only for the quantum gases He, H_2, and D_2.

$$F_Q^\circ = 1.22Q^{0.15} \{1 + 0.00385[(T_r - 12)^2]^{1/M} \, \text{sign} \, (T_r - 12)\}‡ \quad (9\text{-}4.18)$$

where $Q = 1.38$ (He), $Q = 0.76$ (H_2), $Q = 0.52$ (D_2).

Equation (9-4.15) is similar to an equation proposed by Thodos and coworkers (e.g., [225]). It is interesting to note that, if $T_r \leq 1$, the $f(T_r)$ in brackets in Eq. (9-4.15) is closely approximated by $0.606T_r$, that is,

$$\eta\xi \approx (0.606T_r)F_P^\circ F_Q^\circ \qquad T_r \leq 1 \quad (9\text{-}4.19)$$

---

†Actually the definition used by Lucas was $\mu_r = [\mu^2 P_c/(kT_c)^2]$. If μ is expressed in debyes, where 1 debye = 10^{-18} esu·cm = 3.336×10^{-30} C·m, and $(4\pi)(8.854187 \times 10^{-12})C^2 = $ N·m², then, if P_c is in N/m², T_c is in kelvins, and k = Boltzmann's constant = 1.3806×10^{-23} J/K, μ_r is dimensionless. Equation (9-4.16) has been presented with the unit conversions already done and P_c is in bars rather than N/m².

‡sign ( ) indicates that one should use +1 or -1 depending on whether the value of the argument ( ) is >0 or <0.

Thus, when $T_r \leq 1$, low-pressure gas viscosities are essentially proportional to the absolute temperature. This might have been anticipated since, in Fig. 9-2, the slope of log Ω_v versus log T^* is close to -0.5. With $n = -0.5$ in Eq. (9-4.5), it would have been predicted that $\eta \propto T$.

The method of Lucas is illustrated in Example 9-2.

Example 9-2 Estimate the viscosity of methanol vapor at a temperature of 550 K and 1 bar by using Lucas' method. The experimental value is 181 μP [188].

solution From Appendix A, $T_c = 512.6$ K, $P_c = 80.9$ bar, $Z_c = 0.224$, $M = 32.042$, and $\mu = 1.7$ debyes. $T_r = 550/512.6 = 1.07$, and $\mu_r = 52.46[(1.7)^2(80.9)/(512.6)^2] = 4.67 \times 10^{-2}$. From Eq. (9-4.17),

$$F_P^\circ = 1 + (30.55)(0.292 - 0.224)^{1.72} = 1.30$$

With Eq. (9-4.14),

$$\xi = 0.176\left[\frac{512.6}{(32.042)^3(80.9)^4}\right]^{1/6} = 4.71 \times 10^{-3} \ (\mu P)^{-1}$$

Then, with Eq. (9-4.15)

$$\eta\xi = \{(0.807)(1.07)^{0.618} - 0.357 \exp[-(0.449)(1.07)]$$
$$+ 0.340 \exp[-(4.058)(1.07)] + 0.018\}(1.30)$$
$$= 0.836$$

$$\eta = \frac{0.836}{(4.71 \times 10^{-3)})} = 178 \ \mu P$$

$$\text{Error} = \frac{178 - 181}{181} \times 100 = -1.7\%$$

In Table 9-2, experimental viscosities are compared with those computed by Lucas's method. The average absolute error is 3.0 percent. Even with the correction factor F_P°, higher errors are noted for polar compounds compared to nonpolar.

Reichenberg [165, 168] has suggested an alternate corresponding states relation for low-pressure gas viscosity of *organic* compounds.

$$\eta = \frac{M^{1/2}T}{a^*[1 + (4/T_c)][1 + 0.36T_r(T_r - 1)]^{1/6}} \frac{T_r(1 + 270\mu_r^4)}{T_r + 270\mu_r^4} \tag{9-4.20}$$

η is in μP; M is the molecular weight; T is the temperature; T_c is the critical temperature, in kelvins; T_r is the reduced temperature; and μ_r is the reduced dipole moment defined earlier in Eq. (9-4.16). The parameter a^* is defined as

$$a^* = \Sigma N_i C_i \tag{9-4.21}$$

where n_i represents the number of groups of the ith type and C_i is the group contribution shown in Table 9-3.

The term $(1 + 4/T_c)$ in the denominator of Eq. (9-4.20) may be neglected except for treating quantum gases with low values of T_c.

TABLE 9-3 Values of the Group Contributions C_i for the Estimation of a^* in Eq. (9-4.21) [165]

Group	Contribution C_i
—CH$_3$	9.04
$\diagup$CH$_2$ (nonring)	6.47
$\diagup$CH— (nonring)	2.67
$\diagup$C$\diagdown$ (nonring)	−1.53
=CH$_2$	7.68
=CH— (nonring)	5.53
$\diagup$C= (nonring)	1.78
≡CH	7.41
≡C— (nonring)	5.24
$\diagup$CH$_2$ (ring)	6.91
$\diagup$CH— (ring)	1.16
$\diagup$C$\diagdown$ (ring)	0.23
=CH— (ring)	5.90
$\diagup$C= (ring)	3.59
—F	4.46
—Cl	10.06
—Br	12.83
—OH (alcohols)	7.96
$\diagup$O (nonring)	3.59
$\diagup$C=O (nonring)	12.02

TABLE 9-3   Values of the Group Contributions C_i for the Estimation of a^* in Eq. (9-4.21) [165] (Continued)

—CHO (aldehydes)	14.02
—COOH (acids)	18.65
—COO— (esters) or HCOO (formates)	13.41
—NH₂	9.71
⟩NH (nonring)	3.68
=N—(ring)	4.97
—CN	18.13
⟩S (ring)	8.86

A comparison between calculated and experimental low-pressure gas viscosity values is given in Table 9-2, and the method is illustrated in Example 9-3.

Example 9-3 Estimate the viscosity of ethyl acetate vapor at 125°C and low pressure. The experimental value is reported to be 101 μP [129].

solution From Appendix A, $T_c = 523.2$ K, $M = 88.107$, $P_c = 38.3$ bar, and $\mu = 1.9$ debyes. With Eq. (9-4.16),

$$\mu_r = \frac{(52.46)(1.9)^2(38.3)}{(523.2)^2} = 0.0265$$

$T_r = (125 + 273)/523.2 = 0.761$. With Eq. (9-4.21) and Table 9-3,

$$a^* = 2(-CH_3) + (-CH_2) + (-COO-) = (2)(9.04) + 6.47 + 13.41 = 37.96$$

With Eq. (9-4.20),

$$\eta = \frac{(88.107)^{1/2}(125 + 273)}{37.96[1 + (0.36)(0.761)(0.761 - 1)]^{1/6}} \frac{(0.761)[1 + (270)(0.0265)^4]}{0.761 + (270)(0.0265)^4} = 99.4 \ \mu P$$

$$\text{Error} = \frac{99.4 - 101}{101} \times 100 = -1.5\%$$

Recommendations for estimating low-pressure viscosities of pure gases

Any of the three estimation methods described in this section may be used with the expectation of errors of 0.5 to 1.5 percent for nonpolar compounds and 2 to 4 percent for polar compounds. Lucas's method requires

as input data T_c, P_c, and M as well as μ and Z_c for polar compounds and is easy to apply. At present, it is not suitable for highly associated gases like acetic acid, but it could probably be extended by multiplication of an appropriate factor as in the Chung et al.'s technique. Chung et al.'s method requires somewhat more input (T_c, V_c, and M and μ, ω, and κ for the polar correction). The critical volume is less readily available than the critical pressure, and the association factor κ is an empirical constant that must be determined from viscosity data. The method is not suited for quantum gases. Reichenberg's technique requires M, T_c, and structural groups as well as μ for the polar correction. This method is not suitable for inorganic gases and cannot be applied to organic gases for which necessary group contributions have not been determined.

9-5   Viscosities of Gas Mixtures at Low Pressures

The rigorous kinetic theory of Chapman-Enskog can be extended to determine the viscosity of low-pressure multicomponent mixtures [23, 24, 25, 27, 40, 100, 119]. The final expressions are quite complicated and are rarely used to estimate mixture viscosities. Three simplifications of the rigorous theoretical expressions are described below. Reichenberg's equations are the most complex, but, as shown later, the most consistently accurate. Wilke's method is simpler, and that of Herning and Zipperer is even more so. All these methods are essentially interpolative; i.e., the viscosity values for the pure components must be available. The methods then lead to estimations showing how the mixture viscosity varies with composition. Later in this section, two corresponding states methods are described; they do not require pure component values as inputs.

Method of Reichenberg [164, 167, 168]

In this technique, Reichenberg has incorporated elements of the kinetic theory approach of Hirschfelder, Curtiss, and Bird [100] with corresponding states methodology to obtain desired parameters. In addition, a polar correction has been included. The general, multicomponent mixture viscosity equation is:

$$\eta_m = \sum_{i=1}^{n} K_i \left(1 + 2 \sum_{j=1}^{i-1} H_{ij}K_j + \sum_{\substack{j=1 \\ \neq i}}^{n} \sum_{\substack{k=1 \\ \neq i}}^{n} H_{ij}H_{ik}K_jK_k \right) \tag{9-5.1}$$

where η_m is the mixture viscosity and n is the number of components.

With η_i the viscosity of pure i, M_i the molecular weight of i, and y_i the mole fraction of i in the mixture,

$$K_i = \frac{y_i \eta_i}{y_i + \eta_i \sum_{\substack{k=1 \\ \neq i}}^{n} y_k H_{ik}[3 + (2M_k/M_i)]} \tag{9-5.2}$$

Two other component properties used are:

$$U_i = \frac{[1 + 0.36 T_{r_i}(T_{r_i} - 1)]^{1/6} F_{R_i}}{(T_{r_i})^{1/2}} \tag{9-5.3}$$

$$C_i = \frac{M_i^{1/4}}{(\eta_i U_i)^{1/2}} \tag{9-5.4}$$

where $T_{r_i} = T/T_{c_i}$ and F_{R_i} is a polar correction.

$$F_{R_i} = \frac{T_{r_i}^{3.5} + (10\mu_{r_i})^7}{T_{r_i}^{3.5}[1 + (10\mu_{r_i})^7]} \tag{9-5.5}$$

Here μ_{r_i} is the reduced dipole moment of i and is calculated as shown earlier in Eq. (9-4.16). For the term $H_{ij} = H_{ji}$,

$$H_{ij} = \left[\frac{M_i M_j}{32(M_i + M_j)^3} \right]^{1/2} (C_i + C_j)^2 \times \frac{[1 + 0.36 T_{r_{ij}}(T_{r_{ij}} - 1)]^{1/6} F_{R_{ij}}}{(T_{r_{ij}})^{1/2}} \tag{9-5.6}$$

with $\qquad T_{r_{ij}} = \dfrac{T}{(T_{c_i} T_{c_j})^{1/2}} \tag{9-5.7}$

$F_{R_{ij}}$ is found from Eq. (9-5.5) with T_{r_i} replaced by $T_{r_{ij}}$ and μ_{r_i} by $\mu_{r_{ij}} = (\mu_{r_i}\mu_{r_j})^{1/2}$.

For a binary gas mixture of 1 and 2, these equations may be written as:

$$\eta_m = K_1(1 + H_{12}^2 K_2^2) + K_2(1 + 2H_{12}K_1 + H_{12}^2 K_1^2) \tag{9-5.8}$$

$$K_1 = \frac{y_1 \eta_1}{y_1 + \eta_1\{y_2 H_{12}[3 + (2M_2/M_1)]\}} \tag{9-5.9}$$

$$K_2 = \frac{y_2 \eta_2}{y_2 + \eta_2\{y_1 H_{12}[3 + (2M_1/M_2)]\}} \tag{9-5.10}$$

$$U_1 = \frac{[1 + 0.36 T_{r_1}(T_{r_1} - 1)]^{1/6}}{T_{r_1}^{1/2}} \frac{T_{r_1}^{3.5} + 10^7 \mu_{r_1}^7}{T_{r_1}^{3.5}(1 + 10^7\mu_{r_1}^7)} \tag{9-5.11}$$

and a comparable expression for U_2. The meaning of C_1 and C_2 is clear from Eq. (9-5.4). Finally, with

$$T_{r12} = \frac{T}{(T_{c_1} T_{c_2})^{1/2}} \quad \text{and} \quad \mu_{r12} = (\mu_{r_1} \mu_{r_2})^{1/2}$$

$$H_{12} = \frac{(M_1 M_2/32)^{1/2}}{(M_1 + M_2)^{3/2}} \frac{[1 + 0.36 T_{r12}(T_{r12} - 1)]^{1/6}}{(T_{r12})^{1/2}} \tag{9-5.12}$$

$$\times (C_1 + C_2)^2 \frac{T_{r12}^{3.5} + (10\mu_{r12})^7}{T_{r12}^{3.5}[1 + (10\mu_{r12})^7]}$$

To employ Reichenberg's method, for each component one needs the pure gas viscosity at the system temperature as well as the molecular weight, dipole moment, critical temperature, and critical pressure. The temperature and composition are state variables.

The method is illustrated in Example 9-4. A comparison of experimental and calculated gas-mixture viscosities is shown in Table 9-4.

Example 9-4 Use Reichenberg's method to estimate the viscosity of a nitrogen-monochlorodifluoromethane (R-22) mixture at 50°C and atmospheric pressure. The mole fraction nitrogen is 0.286. The experimental viscosity is 145 μP [195].

solution The following pure component properties are used:

	N_2	$CHClF_2$
T_c, K	126.2	369.3
P_c, bar	33.9	49.7
M, g/mol	28.013	86.469
μ, debyes	0	1.4
η, 50°C, μP	188	134

With $T = 50°C$, $T_r (N_2) = 2.56$, and $T_r (CHClF_2) = 0.875$,

$$T_{r12} = \frac{50 + 273.2}{[(126.2)(369.3)]^{1/2}} = 1.497$$

$\mu_r (N_2) = 0$, and, from Eq. (9-4.16)

$$\mu_r (CHClF_2) = \frac{(52.46)(1.4)^2(49.7)}{(369.3)^2} = 0.0375$$

Since $\mu_{r12} = (\mu_{r_1} \mu_{r_2})^{1/2}$, then for this mixture, $\mu_{r12} = 0$. With Eq. (9-5.11), for $CHClF_2$,

$$U (CHClF_2) = \frac{[1 + (0.36)(0.875)(0.875 - 1)]^{1/6}}{(0.875)^{1/2}} \times \frac{(0.875)^{3.5} + (10)^7(0.0375)^7}{(0.875)^{3.5}[1 + (10)^7(0.0375)^7]} = 1.062$$

and $U (N_2) = 0.725$.

Then, $C(N_2) = \dfrac{(28.013)^{1/4}}{[(188)(0.725)]^{1/2}} = 0.197$

and $C(CHClF_2) = 0.256$

Next,

$$H(N_2\text{-}CHClF_2) = (0.197 + 0.256)^2 \dfrac{[(28.013)(86.469)]^{1/2}}{[32(28.013 + 86.469)^3]^{1/2}}$$

$$\times \dfrac{[1 + (0.36)(1.497)(1.497 - 1)]^{1/6}}{(1.497)^{1/2}} \times 1.0$$

$$= 1.237 \times 10^{-3}$$

$$K(N_2) = \dfrac{(0.286)(188)}{0.286 + (188)(0.714)(1.237 \times 10^{-3})\{3 + [(2)(86.469)/28.013]\}}$$

$$= 29.71$$

and $K(CHClF_2) = 107.9$. Substituting into Eq. (9-5.8),

$$\eta_m = (29.71)[1 + (1.237 \times 10^{-3})^2(107.9)^2] +$$

$$(107.9)[1 + (2)(1.237 \times 10^{-3})(29.71) + (1.237 \times 10^{-3})^2(29.71)^2]$$

$$= 146.2 \ \mu P$$

$$\text{Error} = \dfrac{146.2 - 145}{145} \times 100 = 0.8\%$$

Method of Wilke

In a further simplification of the kinetic theory approach, Wilke [221] neglected second-order effects and proposed:

$$\eta_m = \sum_{i=1}^{n} \dfrac{y_i \eta_i}{\sum_{j=1}^{n} y_j \phi_{ij}} \tag{9-5.13}$$

where

$$\phi_{ij} = \dfrac{[1 + (\eta_i/\eta_j)^{1/2}(M_j/M_i)^{1/4}]^2}{[8(1 + M_i/M_j)]^{1/2}} \tag{9-5.14}$$

ϕ_{ji} is found by interchanging subscripts or by

$$\phi_{ji} = \dfrac{\eta_j}{\eta_i}\dfrac{M_i}{M_j}\phi_{ij} \tag{9-5.15}$$

For a binary system of 1 and 2, with Eqs. (9-5.13) to (9-5.15),

$$\eta_m = \dfrac{y_1\eta_1}{y_1 + y_2\phi_{12}} + \dfrac{y_2\eta_2}{y_2 + y_1\phi_{21}} \tag{9-5.16}$$

where η_m = viscosity of the mixture
η_1, η_2 = pure component viscosities
y_1, y_2 = mole fractions

TABLE 9-4 Comparison of Calculated and Experimental Low-Pressure Gas Mixture Viscosities

System	T, K	Mole fraction first component	Viscosity (exp.) μP	Ref.	Reichenberg, Eq. (9-5.8)	Wilke, Eq. (9-5.16)	Herning and Zipperer, Eq. (9-5.17)	Lucas, Eq. (9-4.15) with Eqs. (9-5.18) through (9-5.23)	Chung et al., Eq. (9-5.24)
Nitrogen-hydrogen	373	0.0	104.2	155, 208	—	—	—	0.8	−11
		0.2	152.3		4.3	12	2.0	2.1	−23
		0.51	190.3		1.8	5.6	−1.0	−2.0	−11
		0.80	205.8		0.1	1.4	−1.2	3.6	−3.3
		1.0	210.1		—	—	—	0.4	0
Methane-propane	298	0.0	81.0	18	—	—	—	3.5	1.3
		0.2	85.0		0.2	−0.3	−0.2	4.6	1.7
		0.4	89.9		0.1	−0.8	−0.6	5.0	1.7
		0.6	95.0		0.6	−0.4	−0.2	5.4	1.9
		0.8	102.0		0.2	−0.6	−0.5	3.7	1.0
		1.0	110.0		—	—	—	0.3	1.0
	498	0.0	131.0	18	—	—	—	4.0	2.3
		0.2	136.0		0.4	0.0	−0.2	5.2	2.7
		0.4	142.0		0.6	0.0	−0.5	5.6	2.6
		0.6	149.0		0.7	0.0	−0.6	5.2	2.0
		0.8	157.0		0.7	0.0	−0.3	3.7	1.1
		1.0	167.0		—	—	—	−0.2	0.2
Carbon tetrafluoride–sulfur hexafluoride	303	0.0	159.0	162	—	—	—	6.6	0.7
		0.257	159.9		2.0	2.0	1.8	9.3	3.8
		0.491	161.5		3.4	3.4	3.1	11.0	6.2
		0.754	164.3		4.6	4.6	4.3	13.0	8.4
		1.0	176.7		—	—	—	7.4	5.6
Nitrogen-carbon dioxide	293	0.0	146.6	120	—	—	—	1.6	−1.2
		0.213	153.5		0.5	−1.3	−1.0	0.4	−0.3
		0.495	161.8		0.4	−1.8	−1.5	−0.2	0.7
		0.767	172.1		−2.0	−2.8	−2.5	−1.7	−0.7
		1.0	175.8		—	—	—	0.1	−0.2

Percent deviation† calculated by method of: (spanning the last five columns)

System	No.	x	T	Ref.	% dev†	% dev†	% dev†	% dev†	% dev†
Ammonia–hydrogen	306	0.0	90.6	155	—	—	—	2.4	-9.9
		0.195	118.4		-4.0	-11	-18	-2.7	2.1
		0.399	123.8		-4.6	-12	-19	-3.0	10.0
		0.536	122.4		-4.5	-11	-16	-2.7	10.0
		0.677	120.0		-4.8	-9.7	-14	-3.1	7.1
		1.0	105.9		—	—	—	1.3	0.9
Hydrogen sulfide–ethyl ether	331	0.0	84.5	156	—	—	—	-1.7	-4.0
		0.204	87		-2.9	-3.2	0.2	2.3	0.4
		0.500	97		-2.2	-2.8	3.2	3.4	1.7
		0.802	116		0.0	-0.4	4.2	0.6	-0.7
		1.0	137		—	—	—	-3.0	-4.1
Ammonia–methylamine	423	0.0	130.0	32	—	—	—	-2.1	-8.0
		0.25	134.5		-0.8	-0.3	-0.6	-1.5	-7.5
		0.75	142.2		-1.0	-0.3	-0.7	0.1	-3.4
		1.0	146.0		—	—	—	1.1	1.1
	673	0.0	204.8	32	—	—	—	-4.6	-11
		0.25	212.8		-2.6	-0.7	-0.9	-4.9	-11
		0.75	228.3		-3.1	-0.7	-0.9	-4.7	-9.3
		1.0	236.0		—	—	—	-4.3	-5.4
Nitrogen–monochlorodifluoromethane	323	0.0	134	195	—	—	—	11.0	6.0
		0.286	145		0.8	-0.8	-0.7	11.0	7.3
		0.463	153		1.3	-1.0	-0.8	11.0	7.4
		0.644	164		0.7	-1.8	-1.6	8.9	5.6
		0.824	177		-0.3	-2.2	-2.1	5.0	2.4
		1.0	188		—	—	—	0.8	0.4
Nitrous oxide–sulfur dioxide	353	0.0	152.3	39	—	—	—	3.9	-1.5
		0.325	161.7		-1.7	-2.2	-2.2	0.6	-1.6
		0.625	167.8		-1.6	-2.2	-2.1	-0.6	-2.3
		0.817	170.7		-0.9	-1.3	-1.2	-0.7	-1.9
		1.0	173.0		—	—	—	-0.6	-0.7
Nitrogen–n-heptane	344	0.0	69.4	36,188	—	—	—	0.8	-3.5
		0.515	104.0		0.7	-6.2	11	-0.2	-4.8
		0.853	154.6		0.9	-4.7	7.4	-0.5	-3.2
		1.0	197.5		—	—	—	0.6	0.2

†Percent deviation = [(calc. − exp.)/(exp.)] × 100.

and
$$\phi_{12} = \frac{[1 + (\eta_1/\eta_2)^{1/2}(M_2/M_1)^{1/4}]^2}{\{8[1 + (M_1/M_2)]\}^{1/2}}$$

$$\phi_{21} = \phi_{12}\frac{\eta_2}{\eta_1}\frac{M_1}{M_2}$$

Equation (9-5.13), with ϕ_{ij} from Eq. (9-5.14), has been extensively tested. Wilke [221] compared values with data on 17 binary systems and reported an average deviation of less than 1 percent; several cases in which η_m passed through a maximum were included. Many other investigators have tested this method [4, 28, 42, 51, 78, 161, 176, 177, 191, 214, 223]. In most cases, only nonpolar mixtures were compared, and very good results obtained. For some systems containing hydrogen as one component, less satisfactory agreement was noted. In Table 9-4, Wilke's method predicted mixture viscosities that were larger than experimental for the H_2-N_2 system, but for H_2-NH_3, it underestimated the viscosities. Gururaja et al. [91] found that this method also overpredicted in the H_2-O_2 case but was quite accurate for the H_2-CO_2 system. Wilke's approximation has proved reliable even for polar-polar gas mixtures of aliphatic alcohols [169]. The principal reservation appears to lie in those cases where $M_i \gg M_j$ and $\eta_i \gg \eta_j$.

Example 9-5 Kestin and Yata [124] report that the viscosity of a mixture of methane and n-butane is 93.35 μP at 293 K when the mole fraction of n-butane is 0.303. Compare this result with the value estimated by Wilke's method. For pure methane and n-butane, these same authors report viscosities of 109.4 and 72.74 μP.

solution Let 1 refer to methane and 2 to n-butane. $M_1 = 16.043$ and $M_2 = 58.124$.

$$\phi_{12} = \frac{[1 + (109.4/72.74)^{1/2}(58.124/16.043)^{1/4}]^2}{\{8[1 + (16.043/58.124)]\}^{1/2}} = 2.268$$

$$\phi_{21} = 2.268\frac{72.74}{109.4}\frac{16.043}{58.124} = 0.416$$

$$\eta_m = \frac{(0.697)(109.4)}{0.697 + (0.303)(2.268)} + \frac{(0.303)(72.74)}{0.303 + (0.697)(0.416)}$$

$$= 92.26 \ \mu P$$

$$\text{Error} = \frac{92.26 - 93.35}{93.35} \times 100 = -1.2\%$$

Herning and Zipperer approximation of ϕ_{ij}

As an approximate expression for ϕ_{ij} the following is proposed [98]:

$$\phi_{ij} = \left(\frac{M_j}{M_i}\right)^{1/2} = \phi_{ji}^{-1} \tag{9-5.17}$$

When Eq. (9-5.17) is used with Eq. (9-5.16) to estimate low-pressure binary gas mixture viscosities, quite reasonable predictions are obtained (Table 9-4) except for systems such as H_2-NH_3. The technique is illus-

trated in Example 9-6. Note that Examples 9-5 and 9-6 treat the same problem; each provides a viscosity estimate close to the experimental value. But the ϕ_{12} and ϕ_{21} values employed in the two cases are quite different. Apparently, multiple sets of ϕ_{ij} and ϕ_{ji} work satisfactorily in Eq. (9-5.13).

Example 9-6 Repeat Example 9-5 by using the Herning and Zipperer approximation for ϕ_{ij}.

solution As before, with 1 as methane and 2 as n-butane.

$$\phi_{12} = \left(\frac{58.124}{16.043}\right)^{1/2} = 1.903$$

$$\phi_{21} = \phi_{12}^{-1} = 0.525$$

$$\eta_m = \frac{(0.697)(109.4)}{0.697 + (0.303)(1.903)} + \frac{(0.303)(72.74)}{0.303 + (0.697)(0.525)}$$

$$= 92.82 \ \mu P$$

$$\text{Error} = \frac{92.82 - 93.35}{93.35} \times 100 = -0.6\%$$

Corresponding states methods

In this approach, one employs pure component estimation methods with mixing and combining rules to relate critical and other properties of the mixture to pure component properties and to composition.

Lucas rules

Lucas [135, 137, 138] defined mixture properties as shown below for use in Eqs. (9-4.14) through (9-4.18).

$$T_{c_m} = \sum_i y_i T_{c_i} \tag{9-5.18}$$

$$P_{c_m} = RT_{c_m} \frac{\sum_i y_i Z_{c_i}}{\sum_i y_i V_{c_i}} \tag{9-5.19}$$

$$M_m = \sum_i y_i M_i \tag{9-5.20}$$

$$F_{P_m}^{\circ} = \sum_i y_i F_{P_i}^{\circ} \tag{9-5.21}$$

$$F_{Q_m}^{\circ} = \left(\sum_i y_i F_{Q_i}^{\circ}\right) A \tag{9-5.22}$$

and, letting the subscript H denote the mixture component of highest molecular weight and L the component of lowest molecular weight,

$$A = 1 - 0.01 \left(\frac{M_{\text{H}}}{M_{\text{L}}}\right)^{0.87} \quad \text{for } \frac{M_{\text{H}}}{M_{\text{L}}} > 9 \text{ and } 0.05 < y_{\text{H}} < 0.7; \tag{9-5.23}$$

otherwise, $A = 1$

The method of Lucas does not necessarily lead to the pure component viscosity η_i when all $y_j = 0$ except $y_i = 1$. Thus the method is not interpolative in the same way as are the techniques of Reichenberg, Wilke, and Herning and Zipperer. Nevertheless, as seen in Table 9-4, the method provides reasonable estimates of η_m in most test cases.

Example 9-7 Estimate the viscosity of a binary mixture of ammonia and hydrogen at 33°C and low pressure by using the Lucas corresponding states method.

solution Let us illustrate the method for a mixture containing 67.7 mole percent ammonia. The data required (from Appendix A) are:

	Ammonia	Hydrogen
T_c K	405.5	33.2
P_c, bar	113.5	13.0
Z_c	0.244	0.306
M	17.031	2.016
μ, debyes	1.47	0
T_r	0.755	9.223

Using Eqs. (9-5.18) to (9-5.20), $T_{cm} = 285.2$ K, $P_{cm} = 89.4$ bar, and $M_m = 12.18$. From these values and Eq. (9-4.14), $\xi_m = 6.4720 \times 10^{-3}$ $(\mu P)^{-1}$. With Eq. (9-4.16), μ_r (NH_3) $= 7.825 \times 10^{-2}$ and μ_r (H_2) $= 0$. Then, with Eq. (9-4.17),

$$F_P^{\circ} (NH_3) = 1 + 30.55(0.292 - 0.244)^{1.72}|0.96 + 0.1(0.755 - 0.7)|$$

$$= 1.159$$

$$F_P^{\circ} (H_2) = 1.0$$

$$F_{Pm}^{\circ} = (1.159)(0.677) + (1)(0.323) = 1.107$$

For the quantum correction, with Eq. (9-5.23), since $\dfrac{M_H}{M_L} = \dfrac{17.031}{2.016} = 8.4 < 9$, then $A = 1$. $F_Q^{\circ} (NH_3) = 1.0$, and with Eq. (9-4.18),

$$F_Q^{\circ} (H_2) = (1.22)(0.76)^{0.15}\{1 + 0.00385[(9.223 - 12)^2]^{1/2.016} \times$$

$$\text{sign } (9.223 - 12)\}$$

$$= (1.171)[1 + (0.01061)(-1)] = 1.158$$

$$F_{Qm}^{\circ} = (1.158)(0.323) + (1)(0.677) = 1.051$$

Next, from Eq. (9-4.15) with $T_{rm} = (33 + 273.2)/285.2 = 1.073$

$$\eta_m \xi_m = (0.645)(1.107)(1.051) = 0.750$$

$$\eta_m = \frac{0.750}{6.472 \times 10^{-3}} = 115.9 \ \mu P$$

The experimental value is 120.0 μP; thus

$$\text{Error} = \frac{115.9 - 120.0}{120.0} \times 100 = -3.4\%$$

The viscosity of the ammonia-hydrogen mixture at 33°C is plotted in Fig. 9-4.
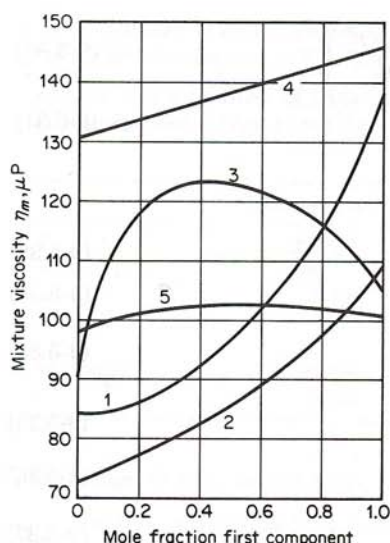
Figure 9-4 Gas mixture viscosities.

No.	System	Reference
1	Hydrogen sulfide–ethyl ether	156
2	Methane–n-butane	124
3	Ammonia–hydrogen	155
4	Ammonia–methyl amine	32
5	Ethylene-ammonia	209

Chung et al. rules [44, 45]

In this case, Eq. (9-3.9) is employed to estimate the mixture viscosity with, however, a factor F_{c_m} as used in Eq. (9-4.9) to correct for shape and polarity.

$$\eta_m = \frac{26.69 F_{c_m}(M_m T)^{1/2}}{\sigma_m^2 \Omega_v} \tag{9-5.24}$$

where $\Omega_v = f(T_m^*)$. In the Chung et al. approach, the mixing rules are:

$$\sigma_m^3 = \sum_i \sum_j y_i y_j \sigma_{ij}^3 \tag{9-5.25}$$

$$T_m^* = \frac{T}{(\epsilon/k)_m} \tag{9-5.26}$$

$$\left(\frac{\epsilon}{k}\right)_m = \frac{\sum_i \sum_j y_i y_j (\epsilon_{ij}/k)\sigma_{ij}^3}{\sigma_m^3} \tag{9-5.27}$$

$$M_m = \left[\frac{\sum_i \sum_j y_i y_j (\epsilon_{ij}/k)\sigma_{ij}^2 M_{ij}^{1/2}}{(\epsilon/k)_m \sigma_m^2}\right]^2 \tag{9-5.28}$$

$$\omega_m = \frac{\sum_i \sum_j y_i y_j \omega_{ij} \sigma_{ij}^3}{\sigma_m^3} \tag{9-5.29}$$

$$\mu_m^4 = \sigma_m^3 \sum_i \sum_j \left(\frac{y_i y_j \mu_i^2 \mu_j^2}{\sigma_{ij}^3} \right) \tag{9-5.30}$$

$$\kappa_m = \sum_i \sum_j y_i y_j \kappa_{ij} \tag{9-5.31}$$

and the combining rules are:

$$\sigma_{ii} = \sigma_i = 0.809 V_{ci}^{1/3} \tag{9-5.32}$$

$$\sigma_{ij} = \xi_{ij}(\sigma_i \sigma_j)^{1/2} \tag{9-5.33}$$

$$\frac{\epsilon_{ii}}{k} = \frac{\epsilon_i}{k} = \frac{T_{ci}}{1.2593} \tag{9-5.34}$$

$$\frac{\epsilon_{ij}}{k} = \zeta_{ij} \left(\frac{\epsilon_i}{k} \frac{\epsilon_j}{k} \right)^{1/2} \tag{9-5.35}$$

$$\omega_{ii} = \omega_i \tag{9-5.36}$$

$$\omega_{ij} = \frac{\omega_i + \omega_j}{2} \tag{9-5.37}$$

$$\kappa_{ii} = \kappa_i \tag{9-5.38}$$

$$\kappa_{ij} = (\kappa_i \kappa_j)^{1/2} \tag{9-5.39}$$

$$M_{ij} = \frac{2M_i M_j}{M_i + M_j} \tag{9-5.40}$$

ξ_{ij} and ζ_{ij} are binary interaction parameters which are normally set equal to unity. The F_{cm} term in Eq. (9-5.24) is defined as in Eq. (9-4.10).

$$F_{cm} = 1 - 0.275\omega_m + 0.059035\mu_{rm}^4 + \kappa_m \tag{9-5.41}$$

where μ_{rm} is given by Eq. (9-4.11)

$$\mu_{rm} = \frac{131.3\mu_m}{(V_{cm} T_{cm})^{1/2}} \tag{9-5.42}$$

$$V_{cm} = (\sigma_m/0.809)^3 \tag{9-5.43}$$

$$T_{cm} = 1.2593 \left(\frac{\epsilon}{k} \right)_m \tag{9-5.44}$$

In these equations, T_c is in kelvins, V_c is in cm^3/mol and μ is in debyes.

The rules suggested by Chung et al. are illustrated for a binary gas mixture in Example 9-8. As with the Lucas approach, the technique is not interpolative between pure component viscosities. Some calculated binary gas mixture viscosities are compared with experimental values in Table 9-4. Errors vary, but they are usually less than about ±5 percent.

Example 9-8   Using Chung et al.'s method, estimate the low-pressure gas viscos-

ity of a binary of hydrogen sulfide and ethyl ether containing 20.4 mole percent H_2S. The temperature is 331 K.

solution For a mixture of hydrogen sulfide and ethyl ether, the following properties are needed (Appendix A):

	Hydrogen sulfide	Ethyl ether
T_c, K	373.2	466.7
V_c, cm^3/mol	98	280
ω	0.109	0.281
μ, debyes	0.9	1.3
κ	0	0
M, g/mol	34.080	74.123
y	0.204	0.796

From Eqs. (9-5.32) and (9-5.33),

$$\sigma \, (H_2S) = (0.809)(98)^{1/3} = 3.730 \text{ Å}$$

$$\sigma \, (EE) = 5.293 \text{ Å}$$

$$\sigma \, (H_2S\text{-}EE) = 4.443 \text{ Å}$$

then, with Eq. (9-5.25),

$$\sigma_m^3 = (0.204)^2(3.730)^3 + (0.796)^2(5.293)^3 + (2)(0.204)(0.796)(4.443)^3$$

$$= 124.58 \text{ Å}^3$$

From Eqs. (9-5.34) and (9-5.35),

$$\frac{\epsilon}{k} \, (H_2S) = \frac{373.2}{1.2593} = 296.4 \text{ K}$$

$$\frac{\epsilon}{k} \, (EE) = 370.6 \text{ K}$$

$$\frac{\epsilon}{k} \, (H_2S\text{-}EE) = 331.4 \text{ K}$$

Then, with Eq. (9-5.27),

$$\left(\frac{\epsilon}{k}\right)_m = [(0.204)^2(296.4)(3.730)^3 + (0.796)^2(370.6)(5.293)^3$$

$$+ \, (2)(0.204)(0.796)(331.4)(4.443)^3]/124.58$$

$$= 360.4 \text{ K}$$

With Eqs. (9-5.28) and (9-5.40),

$$M_m = (\{(0.204)^2(296.4)(3.730)^2(34.080)^{1/2} + (0.796)^2(370.6)(5.293)^2(74.123)^{1/2}$$

$$+ \, (2)(0.204)(0.796)(331.4)(4.443)^2 \, [(2)(34.080)(74.123)/(34.080 + 74.123)]^{1/2}\}$$

$$/(360.4) \, (124.58)^{2/3})^2 = 64.43 \text{ g/mol}$$

With Eq. (9-5.29),

$$\omega_m = \{(0.204)^2(0.109)(3.730)^3 + (0.796)^2(0.281)(5.293)^3$$

$$+ \, (2)(0.204)(0.796)[(0.109 + 0.281)/2](4.443)^3\}/124.58$$

$$= 0.258$$

and with Eq. (9-5.30),

$$\mu_m^4 = \{[(0.204)^2(0.9)^4/(3.730)^3] + [(0.796)^2(1.3)^4/(5.293)^3]$$
$$+ [(2)(0.204)(0.796)(0.9)^2(1.3)^2/(4.443)^3]\}(124.58)$$
$$= 2.218$$
$$\mu_m = 1.22 \text{ debyes}$$

so, with Eqs. (9-5.42) to (9-5.44),

$$V_{cm} = \frac{(124.58)}{(0.809)^3} = 235.3 \text{ cm}^3/\text{mol}$$

$$T_{cm} = (1.2593)(360.4) = 453.9 \text{ K}$$

$$\mu_{rm} = \frac{(131.3)(1.22)}{[(235.3)(453.9)]^{1/2}} = 0.490$$

Since $\kappa_m = 0$, with Eq. (9-5.41),

$$F_{cm} = 1 - (0.275)(0.258) + (0.059035)(0.490)^4 = 0.932$$

Using T_m^* from Eq. (9-5.26) [$= 331/360.4 = 0.918$] and Eq. (9-4.3), $\Omega_v = 1.664$. Finally, with Eq. (9-5.24),

$$\eta_m = \frac{(26.69)(0.932)[(64.43)(331)]^{1/2}}{(124.58)^{2/3}(1.664)}$$
$$= 87.6 \ \mu P$$

The experimental value is 87 μP (Table 9-4).

$$\text{Error} = \frac{87.6 - 87}{87} \times 100 = 0.4\%$$

Discussion and recommendations to estimate the low-pressure viscosity of gas mixtures

As is obvious from the estimation methods discussed in this section, the viscosity of a gas mixture can be a complex function of composition. This is evident from Fig. 9-4. There may be a maximum in mixture viscosity in some cases, e.g., system 3, ammonia-hydrogen. No cases of a viscosity minimum have, however, been reported. Behavior similar to that of the ammonia-hydrogen case occurs most often in polar-nonpolar mixtures in which the pure component viscosities are not greatly different [101, 172]. Maxima are more pronounced as the molecular weight ratio differs from unity.

Of the five estimation methods described in this section, three (Herning and Zipperer, Wilke, and Reichenberg) use the kinetic theory approach and yield interpolative equations between the pure component viscosities. Reichenberg's method is most consistently accurate, but it is the most complex. To use Reichenberg's procedure, one needs, in addition to temperature and composition, the viscosity, critical temperature, critical pressure, molecular weight, and dipole moment of each constituent. Wilke's

and Herning and Zipperer's methods require only the pure component viscosities and molecular weights; these latter two yield reasonably accurate predictions of the mixture viscosity.

Arguing that it is rare to have available the pure gas viscosities at the temperature of interest, both Lucas and Chung et al. provide estimation methods to cover the entire range of composition. At the end points where only pure components exist, their methods reduce to those described earlier in Sec. 9-3. Although the errors from these two methods are, on the average, slightly higher than those of the interpolative techniques, they are usually less than ±5 percent as seen from Table 9-4. Such errors could be reduced even further if pure component viscosity data were available and were employed in a simple linear correction scheme.

Many other estimation methods for determining η_m have been proposed [25, 26, 33, 54, 75, 90, 97, 118, 119, 174, 191, 192, 207, 225], but they were judged either less accurate or less general than those discussed in this section.

It is recommended that Reichenberg's method [Eq. (9-5.8)] be used to calculate η_m if pure component viscosity values are available. Otherwise, either the Lucas method [Eq. (9-4.15)] or the Chung et al. method [Eq. (9-5.24)] can be employed if critical properties are available for all components.

A compilation of references dealing with gas mixture viscosities (low and high pressure) has been prepared by Sutton [193].

9-6 Effect of Pressure on the Viscosity of Pure Gases

The viscosity of a gas is a strong function of pressure near the critical point and at reduced temperatures of about 1 to 2 at high pressures. The complexity of the T-P-η phase diagram is seen in Figs. 9-5 and 9-6 [188]. In Fig. 9-5, the viscosity of carbon dioxide is graphed as a function of temperature with various isobars shown; for CO_2, $T_c = 304.1$ K and $P_c = 73.8$ bar. If the viscosity were plotted as a function of pressure with isotherms, one would have a phase diagram as illustrated in Fig. 9-6 for nitrogen ($T_c = 77.4$ K, $P_c = 33.9$ bar). Lucas [136, 137] has generalized the viscosity phase diagrams (for nonpolar gases) as shown in Fig. 9-7. In this case the ordinate is $\eta\xi$ and the temperatures and pressures are reduced values. ξ is the inverse reduced viscosity defined earlier in Eq. (9-4.14).

In Fig. 9-7, the lower limit of the P_r curves would be indicative of the dilute gas state, as described in Sec. 9-4. In such a state, η increases with temperature. At high reduced pressures, we see there is a wide range of temperatures where η decreases with temperature. In this region the viscosity behavior more closely simulates a liquid state, and, as will be shown in Sec. 9-10, an increase in temperature results in a decrease in viscosity.
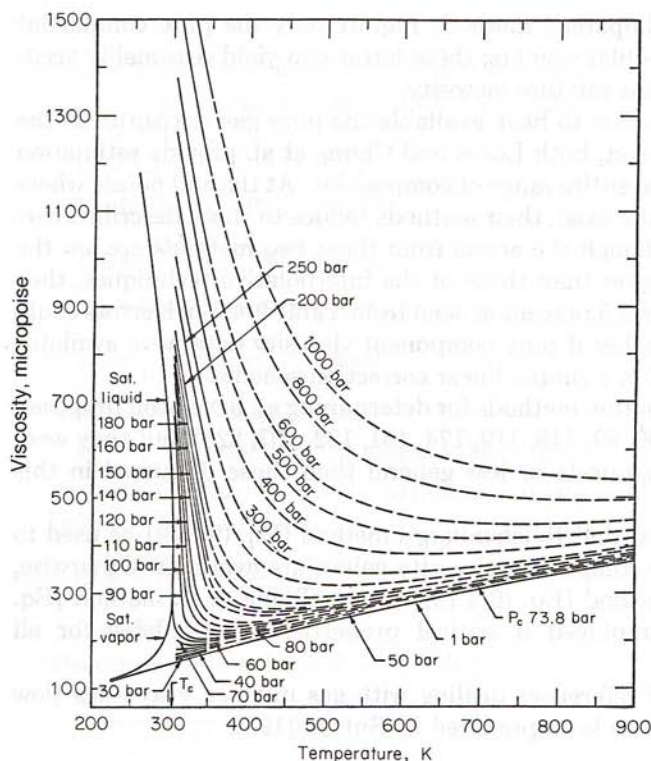
Figure 9-5 Viscosity of carbon dioxide. *(From Stephan and Lucas, Ref. 188.)*

Finally, at very high reduced temperatures, there again results a condition in which pressure has little effect and viscosities increase with temperature.

Enskog dense-gas theory

One of the very few theoretical efforts to predict the effect of pressure on the viscosity of gases is due to Enskog and is treated in detail by Chapman and Cowling [40]. The theory has also been applied to dense gas diffusion coefficients, bulk viscosities, and, for monatomic gases, thermal conductivities. The assumption is made that the gas consists of dense, hard spheres and behaves like a low-density hard-sphere system except that all events occur at a faster rate due to the higher rates of collision [1, 2]. The increase in collision rate is proportional to the radial distribution function Ψ. The Enskog equation for shear viscosity is

$$\frac{\eta}{\eta^\circ} = \Psi^{-1} + 0.8 b_0 \rho + 0.761 \Psi (b_0 \rho)^2 \tag{9-6.1}$$

where η = viscosity, μP
$\quad\quad \eta°$ = low-pressure viscosity, μP
$\quad\quad b_0$ = excluded volume = $\frac{2}{3}\pi N_0 \sigma^3$, cm^3/mol
$\quad\quad N_0$ = Avogadro's number
$\quad\quad \sigma$ = hard-sphere diameter, Å
$\quad\quad \rho$ = molar density, mole/cm^3

And Ψ is the radial distribution function at contact and can be related to an equation of state by

$$\Psi = \frac{Z - 1}{\rho b_0} \qquad (9\text{-}6.2)$$

where Z is the compressibility factor. In the Enskog model, there is no correlation between successive hard-sphere collisions (the molecular chaos approximation). Dymond [61, 62, 63, 64], among others [3, 55, 175], has used molecular dynamics to correct for this deficiency as well as to account for attractive forces. Approaches such as these may lead to reli-
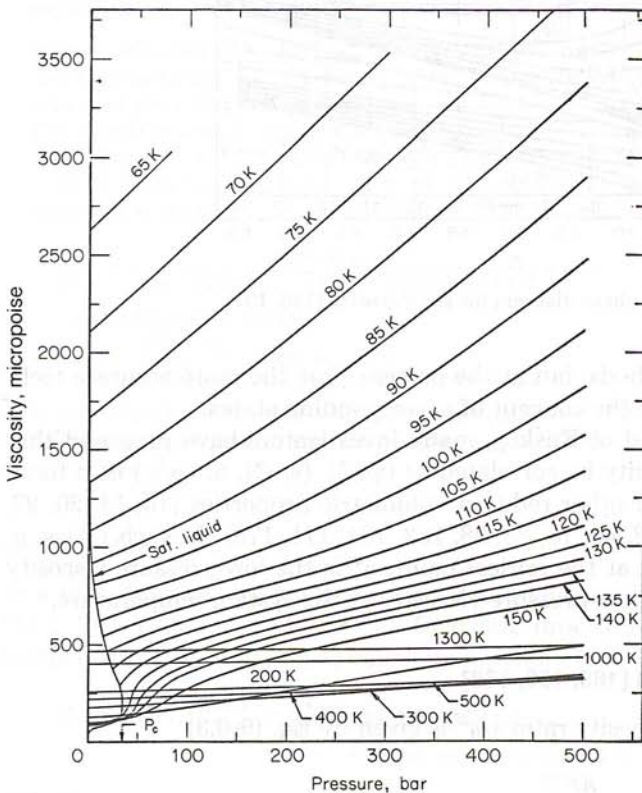
Figure 9-6 Viscosity of nitrogen. *(From Stephan and Lucas, Ref. 188.)*
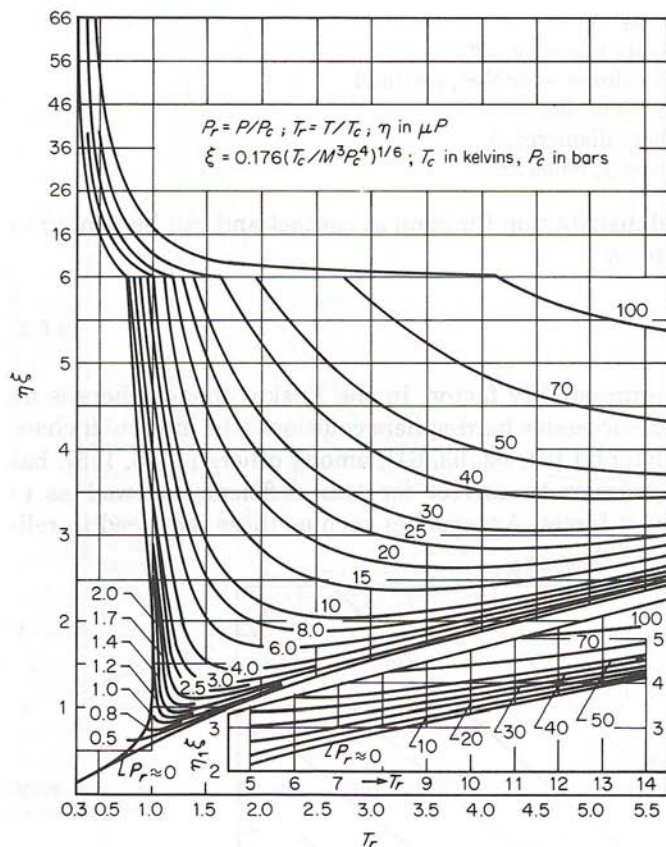
Figure 9-7 Generalized phase diagram for gas viscosity [136, 137].

able predictive methods, but at the present time the more accurate techniques are based on the concept of corresponding states.

Following the lead of Enskog, many investigators have proposed that the dense-gas viscosity be correlated as (η/η°), (η/η_c°), or (η/η_c) as a function of T_r and P_r or other reduced volumetric properties [10, 14, 20, 22, 28, 37, 38, 46, 47, 48, 49, 76, 83, 88, 133, 134, 171, 178]. In such ratios, η_c is the true viscosity at the critical point, η_c° is the low-pressure viscosity at T_c, and η° is the low-pressure viscosity at the system temperature.

Reichenberg method [165, 166, 168]

In this case, the viscosity ratio η/η° is given by Eq. (9-6.3)

$$\frac{\eta}{\eta^\circ} = 1 + Q\,\frac{AP_r^{3/2}}{BP_r + (1 + CP_r^D)^{-1}} \tag{9-6.3}$$

The constants, A, B, C, and D are functions of the reduced temperature T_r:

$$A = \frac{\alpha_1}{T_r} \exp \alpha_2 T_r^a \qquad B = A(\beta_1 T_r - \beta_2)$$

$$C = \frac{\gamma_1}{T_r} \exp \gamma_2 T_r^c \qquad D = \frac{\delta_1}{T_r} \exp \delta_2 T_r^d$$

$\alpha_1 = 1.9824 \times 10^{-3} \quad \alpha_2 = 5.2683 \quad a = -0.5767 \quad \beta_1 = 1.6552$

$\beta_2 = 1.2760 \qquad\qquad \gamma_1 = 0.1319 \quad \gamma_2 = 3.7035 \quad c = -79.8678$

$\delta_1 = 2.9496 \qquad\qquad \delta_2 = 2.9190 \quad d = -16.6169$

and $Q = (1 - 5.655\mu_r)$, where μ_r is defined in Eq. (9-4.16). For nonpolar materials, $Q = 1.0$. Example 9-9 illustrates the application of Eq. (9-6.3), and, in Table 9-6, experimental dense gas viscosities are compared to the viscosities estimated with this method. Errors are generally only a few percent; the poor results for ammonia at 420 K seem to be an anomaly.

Example 9-9 Use Reichenberg's method to estimate the viscosity of n-pentane vapor at 500 K and 101 bar. The experimental value is 546 μP [188].

solution Whereas one could estimate the low-pressure viscosity of n-pentane at 500 K by using the methods described in Sec. 9-4, the experimental value is available (114 μP) [188] and will be used.

The dipole moment of n-pentane is zero, so $Q = 1.0$. From Appendix A, $T_c = 469.7$ K and $P_c = 33.7$ bar. Thus $T_r = (500/469.7) = 1.065$ and $P_r = (101/33.7) = 3.00$. From the definitions of A, B, C, and D given under Eq. (9-6.3), $A = 0.2999$, $B = 0.1458$, $C = 1.271$, and $D = 7.785$. With Eq. (9-6.3),

$$\frac{\eta}{\eta^\circ} = 1 + \frac{(0.2999)(3.00)^{3/2}}{(0.1458)(3.00) + [1 + (1.271)(3.00)^{7.785}]^{-1}} = 4.56$$

$$\eta = (4.56)(114) = 520 \ \mu P$$

$$\text{Error} = \frac{520 - 546}{546} \times 100 = -4.7\%$$

If one refers back to Fig. 9-7, at $T_r = 1.065$ and $P_r = 3.00$, the viscosity is changing rapidly with both temperature and pressure. Thus, an error of only 5% is quite remarkable.

Lucas method

In a technique which, in some aspects, is similar to Reichenberg's, Lucas [135, 136, 137] recommends the following procedure. For the reduced temperature of interest, first calculate a parameter Z_1:

$$Z_1 = [0.807 \ T_r^{0.618} - 0.357 \exp(-0.449 T_r)$$

$$+ 0.340 \exp(-4.058 T_r) + 0.018] F_P^\circ F_Q^\circ \qquad (9\text{-}6.4)$$

Note that, from Eq. (9-4.15), $Z_1 = \eta^\circ \xi$, where η° refers to the low-pressure viscosity.

If $T_r \leq 1.0$ and $P_r < (P_{vp}/P_c)$, then

$$Z_2 = 0.600 + 0.760 P_r^\alpha + (6.990 P_r^\beta - 0.6)(1 - T_r) \tag{9-6.5}$$

with $\alpha = 3.262 + 14.98 P_r^{5.508}$

$$\beta = 1.390 + 5.746 P_r$$

If $(1 < T_r < 40)$ and $(0 < P_r \leq 100)$, then

$$Z_2 = \eta^\circ \xi \left[1 + \frac{a P_r^e}{b P_r^f + (1 + c P_r^d)^{-1}} \right] \tag{9-6.6}$$

where $\eta^\circ \xi$ is found from Eq. (9-6.4). The term multiplying this group is identical to the pressure correction term in Reichenberg's method, Eq. (9-6.3), but the values of the constants are different.

$$a = \frac{a_1}{T_r} \exp a_2 T_r^\gamma$$

$$b = a(b_1 T_r - b_2)$$

$$c = \frac{c_1}{T_r} \exp c_2 T_r^\delta$$

$$d = \frac{d_1}{T_r} \exp d_2 T_r^\epsilon$$

$$e = 1.3088$$

$$f = f_1 \exp f_2 T_r^\zeta$$

and
$$
\begin{array}{lll}
a_1 = 1.245 \times 10^{-3} & a_2 = 5.1726 & \gamma = -0.3286 \\
b_1 = 1.6553 & b_2 = 1.2723 & \\
c_1 = 0.4489 & c_2 = 3.0578 & \delta = -37.7332 \\
d_1 = 1.7368 & d_2 = 2.2310 & \epsilon = -7.6351 \\
f_1 = 0.9425 & f_2 = -0.1853 & \zeta = 0.4489
\end{array}
$$

After computing Z_1 and Z_2, we define

$$Y = \frac{Z_2}{Z_1} \tag{9-6.7}$$

and the correction factors F_P and F_Q,

$$F_P = \frac{1 + (F_P^\circ - 1) Y^{-3}}{F_P^\circ} \tag{9-6.8}$$

$$F_Q = \frac{1 + (F_Q^\circ - 1)[Y^{-1} - (0.007)(\ln Y)^4]}{F_Q^\circ} \tag{9-6.9}$$

where F_P° and F_Q° are low-pressure polarity and quantum factors determined as shown in Eqs. (9-4.17) and (9-4.18). Finally, the dense gas viscosity is calculated as

$$\eta = \frac{Z_2 F_P F_Q}{\xi} \tag{9-6.10}$$

where ξ is defined in Eq. (9-4.14). At low pressures, Y is essentially unity, and $F_P = 1$, $F_Q = 1$. Also Z_2 then equals $\eta^\circ \xi$ so $\eta \to \eta^\circ$, as expected.

The Lucas method is illustrated in Example 9-10, and calculated dense gas viscosities are compared with experimental data in Table 9-6. In Example 9-10 and Table 9-6, the low-pressure viscosity η° was not obtained from experimental data but was estimated by the Lucas method in Sec. 9-4. Except in a few cases, the error was found to be less than 5 percent. The critical temperature, critical pressure, critical compressibility factor, and dipole moment are required, as well as the system temperature and pressure.

Example 9-10 Estimate the viscosity of ammonia gas at 420 K and 300 bar by using Lucas's method. The experimental values of η and η° are 571 and 146 μP [188].

solution From Appendix A, for ammonia, $M = 17.03$, $Z_c = 0.244$, $T_c = 405.5$ K, $P_c = 113.5$ bar, and $\mu = 1.47$ debyes. Thus, $T_r = (420/405.5) = 1.036$ and $P_r = (300/113.5) = 2.643$. From Eq. (9-4.14),

$$\xi = (0.176) \left[\frac{405.5}{(17.03)^3 (113.5)^4} \right]^{1/6} = 4.96 \times 10^{-3} \, (\mu P)^{-1}$$

and, with Eq. (9-4.16),

$$\mu_r = (52.46) \left[\frac{(1.47)^2 (113.5)}{(405.5)^2} \right] = 7.825 \times 10^{-2}$$

$$F_Q^\circ = 1.0$$

and with Eq. (9-4.17),

$$F_P^\circ = 1 + 30.55(0.292 - 0.244)^{1.72} \, |0.96 + (0.1)(1.036 - 0.7)|$$
$$= 1.164$$

From Eq. (9-6.4), $Z_1 = \eta^\circ \xi = 0.7258$

$$\eta^\circ = \frac{0.7258}{4.96 \times 10^{-3}} = 146 \, \mu P$$

The estimation of the low-pressure viscosity of ammonia agrees very well with the experimental value.

Since $T_r > 1.0$, we use Eq. (9-6.6) to determine Z_2. The values of the coefficients are $a = 0.1998$, $b = 8.834 \times 10^{-2}$, $c = 0.9764$, $d = 9.235$, $e = 1.3088$, and $f = 0.7808$. Then,

$$Z_2 = \left\{ 1 + \frac{(0.1998)(2.643)^{1.3088}}{(8.834 \times 10^{-2})(2.643)^{0.7808} + [1 + (0.9764)(2.643)^{9.235}]^{-1}} \right\} (0.7258)$$
$$= (4.776)(0.7258) = 3.466$$

With Eqs. (9-6.7) to (9-6.9),

$$Y = \frac{3.466}{0.7258} = 4.776$$

$$F_P = \frac{1 + (1.164 - 1)(4.776)^{-3}}{1.164} = 0.860$$

$$F_Q = 1.0$$

and, with Eq. (9-6.10),

$$\eta = \frac{(3.466)(0.860)(1.0)}{4.96 \times 10^{-3}} = 601 \ \mu P$$

$$\text{Error} = \frac{601 - 571}{571} \times 100 = 5.2\%$$

The Reichenberg and Lucas methods employ temperature and pressure as the state variables. In most other dense gas viscosity correlations, however, the temperature and density (or specific volume) are used. In those cases, one must have accurate volumetric data or an applicable equation of state to determine the dense gas viscosity. Three different methods are illustrated below.

Method of Jossi, Stiel, and Thodos [116, 190]

In this case the *residual* viscosity, $\eta - \eta°$, is correlated with fluid density. All temperature effects are incorporated in the $\eta°$ term. To illustrate the behavior of the $\eta - \eta°$ function, consider Fig. 9-8, which shows $\eta - \eta°$ for n-butane graphed as a function of density [59]. Note that there does not appear to be any specific effect of temperature over the range shown. At the highest density, 0.6 g/cm³, the reduced density ρ/ρ_c is 2.63. Similar plots for many other substances are available, for example, He, air, O_2, N_2, CH_4 [121]; ammonia [34, 179]; rare gases [178]; diatomic gases [20]; sulfur dioxide [180]; CO_2 [117]; steam [122]; and various hydrocarbons [35, 69, 80, 186, 187]. Other authors have also shown the applicability of a residual viscosity-density correlation [83, 95, 122, 170, 184, 185].

In the Jossi, Stiel, and Thodos method, separate residual viscosity expressions are given for nonpolar and polar gases, but no quantitative criterion is presented to distinguish these classes.

Nonpolar gases [116]

$$[(\eta - \eta°)\xi_T + 1]^{1/4} = 1.0230 + 0.23364\rho_r$$
$$+ 0.58533\rho_r^2 - 0.40758\rho_r^3 + 0.093324\rho_r^4 \quad (9\text{-}6.11)$$

where η = dense gas viscosity, μP

$\eta°$ = low-pressure gas viscosity, μP

ρ_r = reduced gas density $\rho/\rho_c = V_c/V$

ξ_T = the group $(T_c/M^3 P_c^4)^{1/6}$, where T_c is in kelvins and P_c is in atmospheres, $(\mu P)^{-1}$

M = molecular weight, g/mol

This relation is reported by Jossi et al. to be applicable in the range 0.1 $\leq \rho_r < 3$.

Polar gases [190]

$$(\eta - \eta^\circ)\xi_T = 1.656\rho_r^{1.111} \qquad\qquad\qquad \rho_r \leq 0.1 \quad (9\text{-}6.12)$$

$$(\eta - \eta^\circ)\xi_T = 0.0607(9.045\rho_r + 0.63)^{1.739} \quad 0.1 \leq \rho_r \leq 0.9 \quad (9\text{-}6.13)$$

$$\log\{4 - \log[(\eta - \eta^\circ)\xi_T]\} = 0.6439 - 0.1005\rho_r - \Delta \qquad 0.9 \leq \rho_r < 2.6 \quad (9\text{-}6.14)$$

where $\Delta = 0$ when $0.9 \leq \rho_r \leq 2.2$

$$\Delta = (4.75 \times 10^{-4})(\rho_r^3 - 10.65)^2 \qquad \text{when } 2.2 < \rho_r < 2.6 \qquad\qquad (9\text{-}6.15)$$

and $(\eta - \eta^\circ)\xi_T = 90.0$ and 250 at $\rho_r = 2.8$ and 3.0, respectively. The notation used in Eqs. (9-6.12) to (9-6.15) is defined under Eq. (9-6.11). Note that the parameter ξ_T is *not* the same as ξ defined earlier in Eq. (9-4.14).

An example of the Jossi et al. method is shown below, and calculated dense gas viscosities are compared with experimental values in Table 9-6.

Example 9-11 Use the Jossi, Stiel, and Thodos method to estimate the viscosity of isobutane at 500 K and 100 bar. The experimental value is 261 μP [188] and,
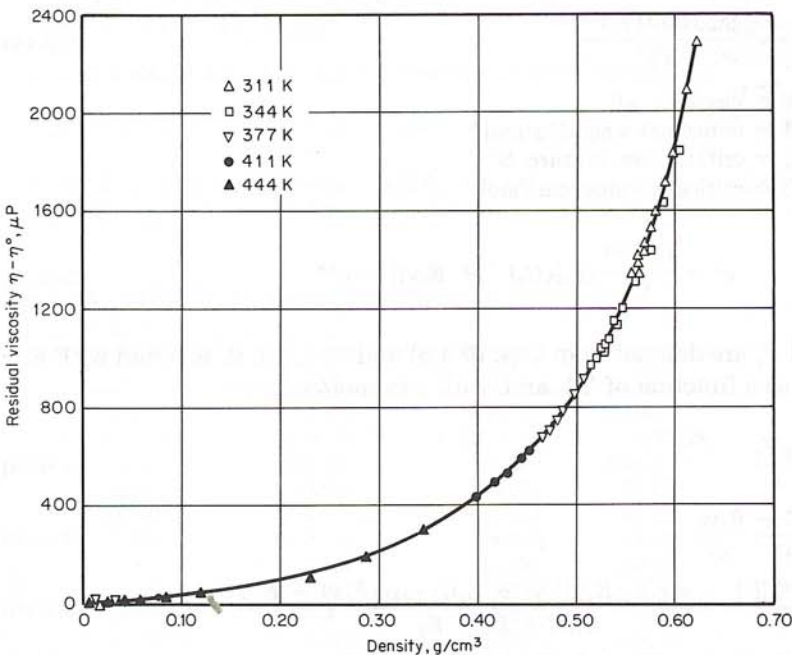
Figure 9-8 Residual n-butane viscosity as a function of density [59].

at 500 K, 100 bar; the specific volume of isobutane is 243.8 cm³/mol [219]. At low pressures, 500 K, $\eta° = 120 \, \mu P$.

solution Since isobutane is nonpolar, Eq. (9-6.11) is used. From Appendix A, T_c = 408.2 K, P_c = 36.5 bar = 36.0 atm, V_c = 263 cm³/mol, and M = 58.12. Then

$$\xi_T = \left[\frac{(408.2)}{(58.12)^3(36.0)^4} \right]^{1/6} = 3.277 \times 10^{-2} \, (\mu P)^{-1}$$

The reduced density = $\rho_r = V_c/V = 263/243.8 = 1.079$. With Eq. (9-6.11),

$$[(\eta - 120)(3.277 \times 10^{-2}) + 1]^{1/4} = 1.0230 + (0.23364)(1.079) + (0.58533)(1.079)^2$$
$$- (0.40758)(1.079)^3 + (0.093324)(1.079)^4$$
$$= 1.571$$
$$\eta = 275 \, \mu P$$

$$\text{Error} = \frac{275 - 261}{261} \times 100 = 5.4\%$$

Chung et al. method [44]

In an extension of the Chung et al. technique to estimate low-pressure gas viscosities, the authors began with Eq. (9-3.9) and employed empirical correction factors to account for the fact that the fluid has a high density. Their relations are shown below.

$$\eta = \eta^* \frac{36.344(MT_c)^{1/2}}{V_c^{2/3}} \tag{9-6.16}$$

where η = viscosity, μP
M = molecular weight, g/mol
T_c = critical temperature, K
V_c = critical volume, cm³/mol

and

$$\eta^* = \frac{(T^*)^{1/2}}{\Omega_v} \{F_c[(G_2)^{-1} + E_6 y]\} + \eta^{**} \tag{9-6.17}$$

T^* and F_c are defined as in Eqs. (9-4.8) and (9-4.10). Ω_v is found with Eq. (9-4.3) as a function of T^*, and, with ρ in mol/cm³,

$$y = \frac{\rho V_c}{6} \tag{9-6.18}$$

$$G_1 = \frac{1 - 0.5y}{(1 - y)^3} \tag{9-6.19}$$

$$G_2 = \frac{E_1\{[1 - \exp(-E_4 y)]/y\} + E_2 G_1 \exp(E_5 y) + E_3 G_1}{E_1 E_4 + E_2 + E_3} \tag{9-6.20}$$

$$\eta^{**} = E_7 y^2 G_2 \exp[E_8 + E_9(T^*)^{-1} + E_{10}(T^*)^{-2}] \tag{9-6.21}$$

and the parameters E_1 to E_{10} are given in Table 9-5 as linear functions of ω (the acentric factor), μ_r^4 [as defined in Eq. (9-4.11)], and the association factor κ (see Table 9-1). One might note that, at very low densities, y approaches zero, G_1 and G_2 approach unity, and η^{**} is negligible. At these limiting conditions, combining Eqs. (9-6.16) and (9-6.17) and (9-4.8) leads to Eq. (9-4.9), which then applies for estimating η°.

The application of the Chung et al. method is shown in Example 9-12. Some calculated values of η are compared with experimental results in Table 9-6. The agreement is quite good and errors usually are below 5%.

Example 9-12 With the Chung et al. method, estimate the viscosity of ammonia at 520 K and 600 bar. The experimental value of η is 466 μP [188]. At this temperature, η° = 182 μP. The specific volume of ammonia at 520 K and 600 bar is 48.2 cm^3/mol [93].

solution From Appendix A, T_c = 405.5 K, V_c = 72 cm^3/mol, ω = 0.250, M = 17.03, and μ = 1.47 debyes. Thus

T_r = 520/405.5 = 1.282 and ρ = 1/48.2 = 2.07 × 10^{-2} mol/cm^3.

With Eq. (9-4.11),

$$\mu_r = \frac{(131.3)(1.47)}{[(72)(405.5)]^{1/2}} = 1.13$$

and with Eq. (9-4.10),

$$F_c = 1 - (0.2756)(0.250) + (0.059035)(1.13)^4 = 1.208$$
$$T^* = (1.2593)(1.282) = 1.615$$

and with Eq. (9-4.3), Ω_v = 1.275. Using Eqs. (9-6.18) and (9-6.19),

$$y = \frac{(2.075 \times 10^{-2})(72)}{6} = 0.249 \quad \text{and} \quad G_1 = 2.067$$

From Table 9-5, the following coefficients were computed: E_1 = −64.82, E_2 = −9.218 × 10^{-3}, E_3 = −204.2, E_4 = 2.430, E_5 = −1.609, E_6 = 3.045, E_7 = 6.839,

TABLE 9-5   Chung et al. Coefficients to Calculate E_i

$E_i = a_i + b_i\omega + c_i\mu_r^4 + d_i\kappa$

i	a_i	b_i	c_i	d_i
1	6.324	50.412	−51.680	1189.0
2	1.210 × 10^{-3}	−1.154 × 10^{-3}	−6.257 × 10^{-3}	0.03728
3	5.283	254.209	−168.48	3898.0
4	6.623	38.096	−8.464	31.42
5	19.745	7.630	−14.354	31.53
6	−1.900	−12.537	4.985	−18.15
7	24.275	3.450	−11.291	69.35
8	0.7972	1.117	0.01235	−4.117
9	−0.2382	0.06770	−0.8163	4.025
10	0.06863	0.3479	0.5926	−0.727

TABLE 9-6 Comparison of Experimental and Calculated Dense Gas Viscosities

Compound	T, K	P, bar	V, cm³/mole	Ref.	η, μP	η°, μP	Ref.	Percent error by method of				
								Reichenberg, Eq. (9-6.3)	Lucas, Eq. (9-6.10)	Jossi et al., Eq. (9-6.11)	Chung et al., Eq. (9-6.16) Table 9-5	Brulé and Starling, Eq. (9-6.16) Table 9-7
Oxygen	300	30.4	806.1	189	212.8	207.2	188	-1.0	-1.6	0.6	-1.5	0.2
		81.0	295.3		225.7			-1.2	-1.1	-0.6	-1.9	0.8
		152.0	155.3		250.3			-0.3	-0.2	-0.8	-0.2	1.6
		304.0	81.4		319.3			3.6	0.8	2.8	3.9	4.6
Methane	200	40.0	282.0	84	90	78.0	188	7.0	0.6	5.9	3.5	1.7
		100.0	60.2		296			10.0	8.2	5.1	3.1	14
		200.0	51.1		415			3.8	5.0	-0.5	-2.2	16
	500	40	1039.0	84	180	177	188	-0.4	-5.6	0.9	-5.3	-3.8
		100	417.7		187			-0.6	-5.1	0.3	-7.2	-2.3
		200	213.7		204			-1.0	-5.0	-0.5	-2.9	-1.0
		500	98.9		263			1.5	-3.3	3.3	2.5	5.3
Isobutane	500	20	2396.0	219	127	120	188	0.9	6.3	0.2	0.8	2.2
		50	620.0		146			5.7	12.0	4.5	9.3	12
		100	244.0		261			-5.2	3.8	5.4	5.5	8.6
		200	159.0		506			-11	2.3	-9.0	-7.2	-5.0
		400	130.0		794			-19	-8.2	-16	-10	-9.9

Substance	T	P										
Ammonia	420	50	588	93	149	146	188	3.0	-2.4	1.7	3.1	-5.2
		150	61.9		349			-17	-6.5	-15	-13	5.1
		300	39.8		571			-21	5.2	3.6	-4.0	22
		600	34.3		752			-24	7.8	11	-1.3	31
	520	50	807.6	93	185	182	188	0.7	-5.8	0.5	-0.1	-9.2
		150	229.6		196			4.5	0.9	2.3	4.0	1.6
		300	90.7		296			-1.4	5.3	-2.5	0.7	13
		600	48.2		466			-13	5.8	-3.2	-3.4	12
Carbon dioxide	360	50	514.6	11	190	177	188	3.0	3.1	1.9	1.1	2.4
		100	211.2		230			2.1	3.3	0.8	3.6	6.1
		400	55.0		730			1.3	7.7	-3.5	-0.8	1.2
		800	45.8		1104			-7.0	1.1	-9.6	-2.2	-1.3
	500	50	802.8	11	243	235	188	0.0	3.0	1.3	0.7	1.6
		100	389.2		254			1.7	5.1	1.4	3.3	5.3
		400	97.1		411			9.8	7.4	2.6	3.6	9.4
		800	62.9		636			10	9.6	0.9	-3.2	2.8
n-Pentane	600	20.3	2240	52	143	134	188	0.0	1.4	0.0	1.2	2.1
		81.1	418.3		242			-7.5	-5.3	-11	-4.6	-1.0
		152	237.5		382			0.9	2.3	-7.9	-7.0	-3.7

†Percent error = [(calc. − exp.)/exp.] × 100

$E_8 = 1.097$, $E_9 = -1.544$, and $E_{10} = 1.116$. Then, with Eq. (9-6.20), $G_2 = 1.494$ and, from Eq. (9-6.21), $\eta^{**} = 1.118$.

Finally, using Eqs. (9-6.17) and (9-6.16),

$$\eta^* = \frac{(1.615)^{1/2}}{1.275} (1.208)[(1.494)^{-1} + (3.045)(0.249)] + 1.118$$

$$= 2.579$$

$$\eta = \frac{(2.579)(36.344)[(17.03)(405.5)]^{1/2}}{(72)^{2/3}}$$

$$= 450 \ \mu P$$

$$\text{Error} = \frac{450 - 466}{466} \times 100 = -3.4\%$$

Brulé and Starling Method [30]

In a manner identical in form with that of Chung et al., Brulé and Starling propose a different set of coefficients for E_1 to E_{10}. These are shown in Table 9-7. Note that no polarity terms are included and the *orientation* parameter γ has replaced the acentric factor ω. If values of γ are not available, the acentric factor may be substituted.

The Brulé and Starling technique was developed to be more applicable for heavy hydrocarbons rather than for simple molecules as tested in Table 9-6.

Discussion and recommendations for estimating dense gas viscosities

Five estimation techniques were discussed in this section. Two (Reichenberg's and Lucas's) were developed to use temperature and pressure as

TABLE 9-7   Brulé and Starling Coefficients to Calculate E_i

$E_i = a_i + b_i\gamma$

i	a_i	b_i
1	17.450	34.063
2	-9.611×10^{-4}	7.235×10^{-3}
3	51.043	169.46
4	-0.6059	71.174
5	21.382	-2.110
6	4.668	-39.941
7	3.762	56.623
8	1.004	3.140
9	-7.774×10^{-2}	-3.584
10	0.3175	1.1600

Note: If γ values are not available, use ω, the acentric factor, or, preferably, obtain from multiproperty analysis by using vapor pressure data [30].

the input variables to estimate the viscosity. The other three required temperature and density; thus, an equation of state would normally be required to obtain the necessary volumetric data if not directly available. In systems developed to estimate many types of properties, it would not be difficult to couple the PVT and viscosity programs to provide densities when needed. In fact, the Brulé and Starling method [30] is predicated on combining thermodynamic and transport analyses to obtain the characterization parameters most suitable for both types of estimations.

Another difference to be recognized among the methods noted in this section is that Reichenberg's and Jossi et al.'s methods require a low-pressure viscosity at the same temperature. The other techniques bypass this requirement and have imbedded into the methods a low-pressure estimation method; i.e., at low densities they reduce to techniques as described in Sec. 9-4. If the Lucas, Chung et al., or Brulé-Starling method were selected, no special low-pressure estimation method would have to be included in a property estimation package.

With these few remarks, along with the testing in Table 9-6 as well as evaluations by authors of the methods, we recommend that either the Lucas or Chung et al. procedure be used to estimate dense (and dilute) gas viscosities of both polar and nonpolar compounds. The Brulé-Starling method is, however, preferable when complex hydrocarbons are of interest, but even for those materials, the Chung et al. procedure should be used at low reduced temperatures ($T_r < 0.5$).

Except when one is working in temperature and pressure ranges in which viscosities are strong functions of these variables (see Fig. 9-7), errors for the recommended methods are usually only a few percent. Near the critical point and in regions where the fluid density is approaching that of a liquid, higher errors may be encountered.

9-7 Viscosity of Gas Mixtures at High Pressures

The most convenient method to estimate the viscosity of dense gas mixtures is to combine, where possible, techniques given previously in Secs. 9-5 and 9-6.

Lucas Approach [135, 136, 137]

In the (pure) dense gas viscosity approach suggested by Lucas, Eqs. (9-6.4) to (9-6.10) were used. To apply this technique to mixtures, rules must be chosen to obtain T_c, P_c, M, and μ as functions of composition. For T_c, P_c, and M of the mixture, Eqs. (9-5.18) to (9-5.20) should be used. The polarity (and quantum) corrections are introduced by using Eqs. (9-6.8) and (9-6.9), where F_P° and F_Q° refer to mixture values from Eqs. (9-5.21)

and (9-5.22). The parameter Y in Eqs. (9-6.8) and (9-6.9) must be based on T_{c_m} and P_{c_m}. F_P° and F_Q°, for the pure components, were defined in Eqs. (9-4.17) and (9-4.18).

Chung et al. approach [44]

To use this method for dense gas mixtures, Eqs. (9-6.16) to (9-6.21) are used. The parameters T_c, V_c ω, M, μ, and κ in these equations are given as functions of composition in Sec. 9-5. That is,

Parameter	Equations to use
T_{c_m}	(9-5.44), (9-5.27)
V_{c_m}	(9-5.43), (9-5.25)
ω_m	(9-5.29), (9-5.25)
M_m	(9-5.28), (9-5.27), and (9-5.25)
μ_m	(9-5.30), (9-5.25)
κ_m	(9-5.31)

Discussion

Both the Lucas and Chung et al. methods utilize the relations for the estimation of dense gas viscosity and apply a *one-fluid* approximation to relate the component parameters to composition. In the Lucas method, the state variables are T, P, and composition, whereas in the Chung et al. procedure, T, ρ, and composition are used. Similar, but less accurate, methods also have been proposed [54, 80].

The accuracy of the Lucas and Chung et al. forms is somewhat less than when applied to pure, dense gases. Also, as noted at the end of Sec. 9-6, the accuracy is often poor when working in the critical region or at densities approaching those of a liquid at the same temperature. The paucity of accurate high-pressure gas mixture viscosity data has limited the testing that could be done, but Chung et al. [44] report absolute average deviations of 8 to 9 percent for both polar and nonpolar dense gas mixtures. A comparable error would be expected from the Lucas form.

As a final comment to the first half of this chapter, it should be noted that, if one were planning a property estimation *system* for use on a high-speed computer, it is recommended that the Lucas, Chung et al., or Brulé and Starling method be used in the dense gas mixture viscosity correlations. Then, at low pressures or for pure components, the relations simplify directly to those described in Secs. 9-4 to 9-6. In other words, it is not necessary—when using these particular methods—to program separate relations for low-pressure pure gases, low-pressure gas mixtures, and high-pressure pure gases. One program is sufficient to cover all those cases

as well as high-pressure gas mixtures. Ely and Hanley [70, 71] have also proposed a general viscosity estimation method.

9-8 Liquid Viscosity

Most gas and gas mixture estimation techniques for viscosity are modifications of theoretical expressions described briefly in Secs. 9-3 and 9-5. There is no comparable theoretical basis for the estimation of liquid viscosities.

The viscosities of liquids are larger than those of gases at the same temperature. As an example, in Fig. 9-9, the viscosities of liquid and vapor benzene are plotted as functions of temperature. Near the normal boiling point (353.4 K), the liquid viscosity is about 36 times the vapor viscosity, and at lower temperatures, this ratio increases even further. Two vapor
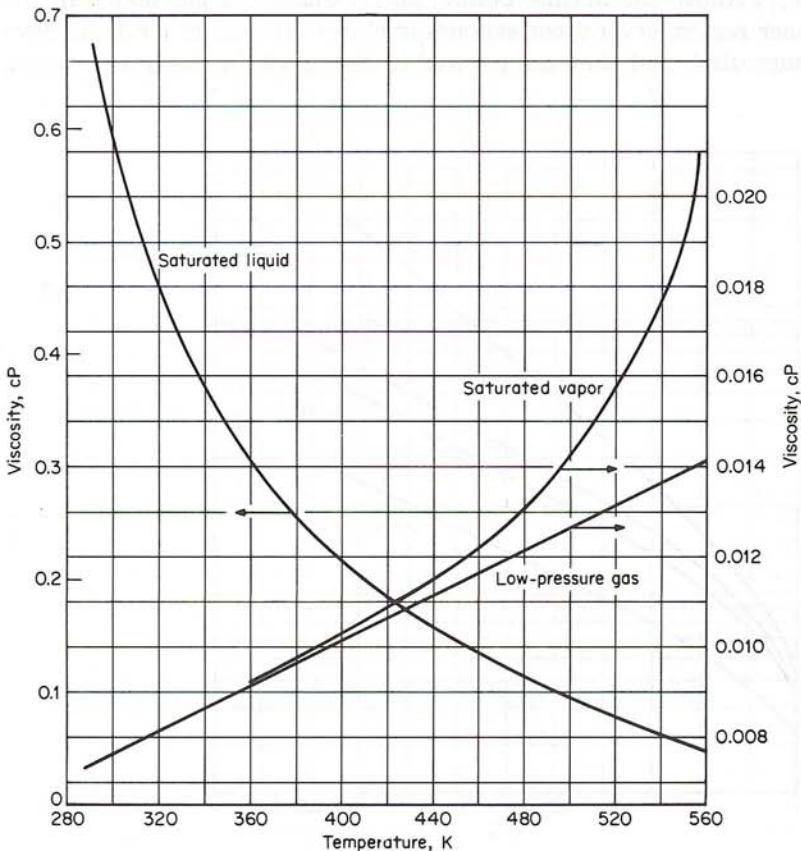
Figure 9-9 Viscosities of liquid and vapor benzene. (T_b = 353.4 K; T_c = 562.2 K).

viscosities are shown in Fig. 9-9. The low-pressure gas line would correspond to vapor at about 1 bar. As noted earlier in Eq. (9-4.19), below T_c, low-pressure gas viscosities vary in a nearly linear manner with temperature. The curve noted as *saturated vapor* reflects the effect of the increase in vapor pressure at higher temperatures. The viscosity of the saturated vapor should equal that of the saturated liquid at the critical temperature (for benzene, $T_c = 562.2$ K).

Much of the curvature in the liquid viscosity–temperature curve may be eliminated if the logarithm of the viscosity is plotted as a function of reciprocal (absolute) temperature. This change is illustrated in Fig. 9-10 for four saturated liquids: ethanol, benzene, n-heptane, and nitrogen. (To allow for variations in the temperature range, the reciprocal of the reduced temperature is employed.) Typically, the normal boiling point would be at a value of $T_r^{-1} \approx 1.5$. For temperatures below the normal boiling point ($T_r^{-1} > 1.5$), the logarithm of the viscosity varies linearly with T_r^{-1}. Above the normal boiling point, this no longer holds. In the nonlinear region, several corresponding states estimation methods have been suggested, and they are covered in Sec. 9-12. In the linear region,
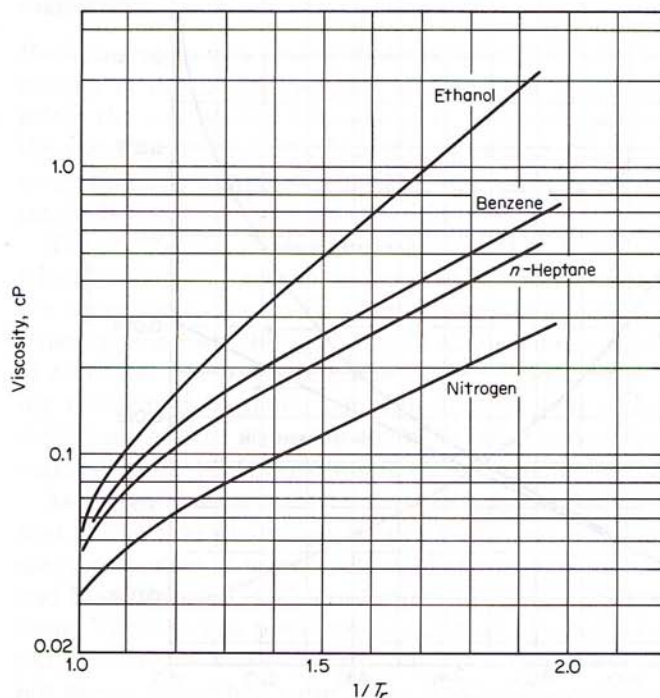
Figure 9-10 Viscosities of various liquids as functions of temperature [188].

most corresponding states methods have not been found to be accurate, and many estimation techniques employ a group contribution approach to emphasize the effects of the chemical structure on viscosity. The curves in Fig. 9-10 suggest that, at comparable reduced temperatures, viscosities of polar fluids are higher than those of nonpolar liquids such as hydrocarbons, which themselves are larger than those of simple molecules such as nitrogen. If one attempts to replot Fig. 9-10 by using a nondimensional viscosity such as $\eta \xi$ [see, for example, Eqs. (9-4.12) to (9-4.14)] as a function of T_r, the separation between curves diminishes, especially at $T_r > 0.7$. However, at lower values of T_r, there are still significant differences between the example compounds.

In the use of viscosity in engineering calculations, one is interested not in the dynamic viscosity, but, rather, in the ratio of the dynamic viscosity to the density. This quantity, called the *kinematic viscosity*, would normally be expressed in m^2/s or in stokes. One stoke (St) is equivalent to 10^{-4} m^2/s. When working with the kinematic viscosity ν, this property
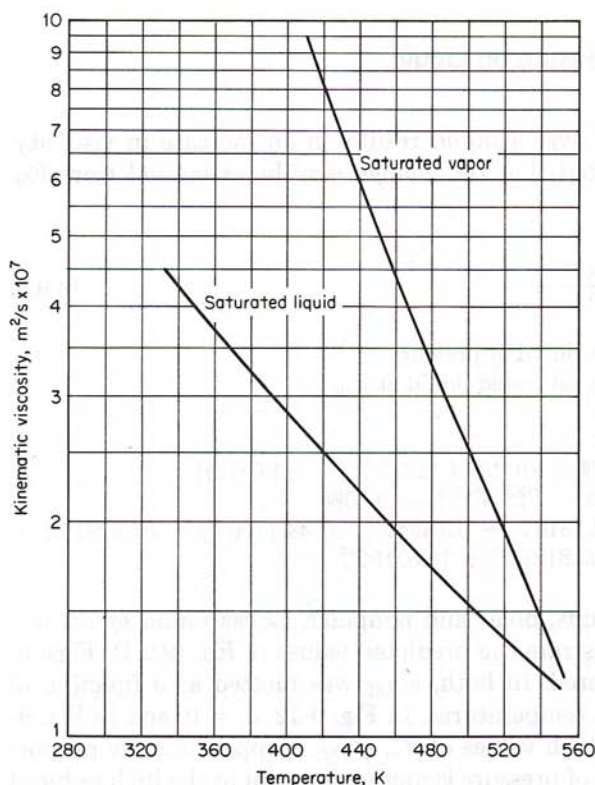
Figure 9-11 Kinematic viscosities of saturated liquid and vapor benzene ($T_b = 353.4$ K; $T_c = 562.2$ K).

decreases in a manner such that ln ν is nearly linear in temperature for both the saturated liquid and vapor as illustrated in Fig. 9-11 for benzene. As with the dynamic viscosity, the kinematic viscosity of the saturated vapor and liquid become equal at the critical point.

The behavior of the kinematic viscosity with temperature has led to several correlation schemes to estimate ν rather than η. However, in most instances, ln ν is related to T^{-1} rather than T. If Fig. 9-11 is replotted by using T^{-1}, again there is a nearly linear correlation with some curvature near the critical point (as there is in Fig. 9-10).

In summary, pure liquid viscosities at high reduced temperatures are usually correlated with some variation of the law of corresponding states (Sec. 9-12). At lower temperatures, most methods are empirical and involve a group contribution approach (Sec. 9-11). Current liquid *mixture* correlations are essentially mixing rules relating pure component viscosities to composition (Sec. 9-13). Little theory has been shown to be applicable to estimating liquid viscosities [9, 27, 31, 79, 100].

9-9   Effect of High Pressure on Liquid Viscosity

Increasing the pressure over a liquid results in an increase in viscosity. Lucas [136] has suggested that the change may be estimated from Eq. (9-9.1).

$$\frac{\eta}{\eta_{SL}} = \frac{1 + D\,(\Delta P_r/2.118)^A}{1 + C\omega\,\Delta P_r} \tag{9-9.1}$$

where η = viscosity of the liquid at pressure
η_{SL} = viscosity of the saturated liquid at P_{vp}
$\Delta P_r = (P - P_{vp})/P_c$
ω = acentric factor
$A = 0.9991 - [4.674 \times 10^{-4}/(1.0523T_r^{-0.03877} - 1.0513)]$
$D = [0.3257/(1.0039 - T_r^{2.573})^{0.2906}] - 0.2086$
$C = -0.07921 + 2.1616T_r - 13.4040T_r^2 + 44.1706T_r^3 - 84.8291T_r^4 + 96.1209T_r^5 - 59.8127T_r^6 + 15.6719T_r^7$

In a test with 55 liquids, polar and nonpolar, Lucas found errors less than 10 percent. To illustrate the predicted values of Eq. (9.9.1), Figs. 9-12 and 9-13 were prepared. In both, η/η_{SL} was plotted as a function of ΔP_r for various reduced temperatures. In Fig. 9-12, $\omega = 0$, and in Fig. 9-13, $\omega = 0.2$. Except at high values of T_r, η/η_{SL} is approximately proportional to ΔP_r. The effect of pressure is more important at the high reduced temperatures. As the acentric factor increases, there is a somewhat smaller effect of pressure. The method is illustrated in Example 9-13.

Example 9-13 Estimate the viscosity of liquid methylcyclohexane at 300 K and 500 bar. The viscosity of the saturated liquid at 300 K is 0.68 cP, and the vapor pressure is less than 1 bar.

solution From Appendix A, $T_c = 572.2$ K, $P_c = 34.7$ bar, and $\omega = 0.236$. Thus, $T_r = 300/572.2 = 0.524$ and $\Delta P_r = 500/34.7 = 14.4$. ($P_{vp}$ was neglected.) Then

$$A = 0.9991 - \frac{4.674 \times 10^{-4}}{(1.0523)(0.524)^{-0.03877} - 1.0513}$$

$$= 0.9822$$

$$D = \frac{0.3257}{[1.0039 - (0.524)^{2.573}]^{0.2906}} - 0.2086$$

$$= 0.1371$$

$$C = -0.07921 + (2.1616)(0.524) - (13.4040)(0.524)^2$$
$$+ (44.1706)(0.524)^3 - (84.8291)(0.524)^4 + (96.1209)(0.524)^5$$
$$- (59.8127)(0.524)^6 + (15.6719)(0.524)^7$$

$$= 0.0619$$
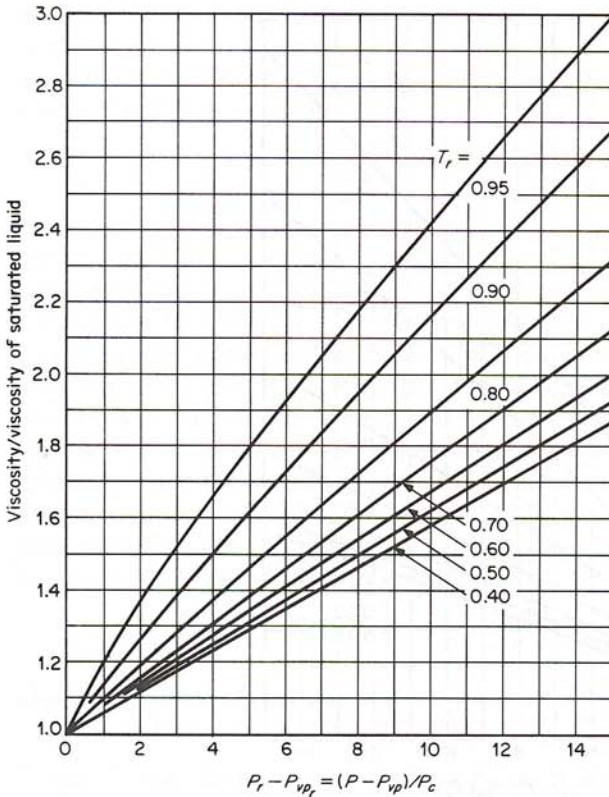
Figure 9-12 Effect of pressure on the viscosity of liquids; $\omega = 0$.

With Eq. (9-9.1),

$$\frac{\eta}{\eta_{SL}} = \frac{1 + (0.1371)(14.4/2.118)^{0.9822}}{1 + (0.236)(14.4)(0.0619)} = 1.57$$

$$\eta = (1.57)(0.68) = 1.07 \text{ cP}$$

The experimental value of η at 300 K and 500 bar is 1.09 cP [188].

$$\text{Error} = \frac{1.07 - 1.09}{1.09} \times 100 = -1.8\%$$

Whereas the correlation by Lucas would encompass most pressure ranges, at pressures over several thousand bar the data of Bridgman suggest that the *logarithm* of the viscosity is proportional to pressure and that the structural complexity of the molecule becomes important. Those who are interested in such high-pressure regions should consult the original publications of Bridgman [21] and others [12, 19, 65, 66, 68, 85, 110, 111, 115, 128, 132, 163].
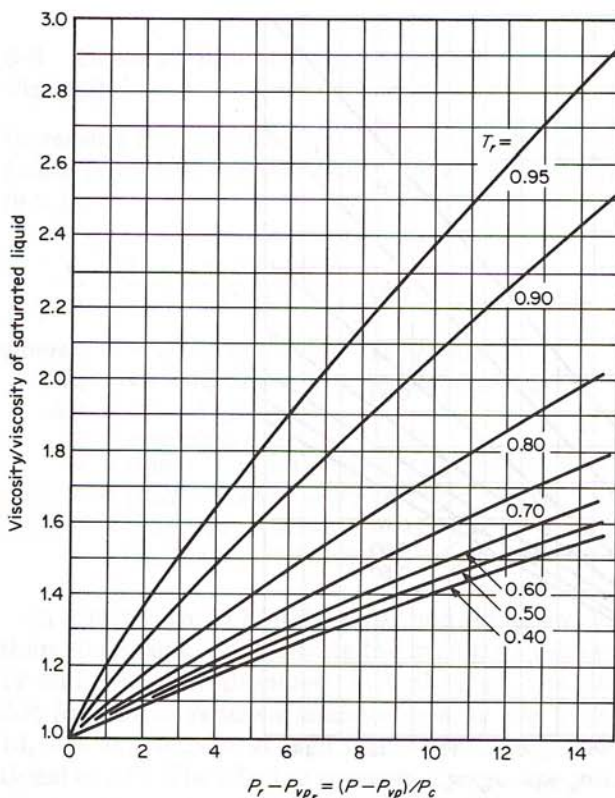
Figure 9-13 Effect of pressure on the viscosity of liquids; $\omega = 0.2$.

9-10   Effect of Temperature on Liquid Viscosity

The viscosities of liquids decrease with increasing temperature either under isobaric conditions or as saturated liquids. This behavior can be seen in Fig. 9-9, where, for example, the viscosity of saturated liquid benzene is graphed as a function of temperature. Also, as noted in Sec. 9-8 and illustrated in Fig. 9-10, for a temperature range from the freezing point to somewhere around the normal boiling temperature, it is often a good approximation to assume ln η_L is linear in reciprocal absolute temperature; i.e.,

$$\ln \eta_L = A + \frac{B}{T} \tag{9-10.1}$$

This simple form was apparently first proposed by de Guzman [53, 153] in 1913, but it is more commonly referred to as the *Andrade* equation [7, 8]. Variations of Eq. (9-10.1) have been proposed to improve upon its correlation accuracy; many include some function of the liquid molar volume in either the A or B parameter [17, 50, 72, 81, 92, 103, 142, 144, 145, 146, 147, 201, 213]. Another variation involves the use of a third constant to obtain the *Vogel* equation [216],

$$\ln \eta_L = A + \frac{B}{T + C} \tag{9-10.2}$$

Goletz and Tassios [82] have used this form (for the kinematic viscosity) and report values of A, B, and C for many pure liquids.

Equation (9-10.1) requires at least two viscosity-temperature datum points to determine the two constants. If only one datum point is available, one of the few ways to extrapolate this value is to employ the approximate Lewis-Squires chart [131], which is based on the empirical fact that the sensitivity of viscosity to temperature variations appears to depend primarily upon the value of the viscosity. This chart, shown in Fig. 9-14, can be used by locating the known value of viscosity on the ordinate and then extending the abscissa by the required number of degrees to find the new viscosity. Figure 9-14 can be expressed in an equation form as

$$\eta_L^{-0.2661} = \eta_K^{-0.2661} + \frac{T - T_K}{233} \tag{9-10.3}$$

where η_L = liquid viscosity at T, cP

η_K = known value of liquid viscosity at T_K, cP

T and T_K may be expressed in either °C or K. Thus, given a value of η_L at T_K, one can estimate values of η_L at other temperatures. Equation (9-10.3) or Fig. 9-14 is only approximate, and errors of 5 to 15 percent (or
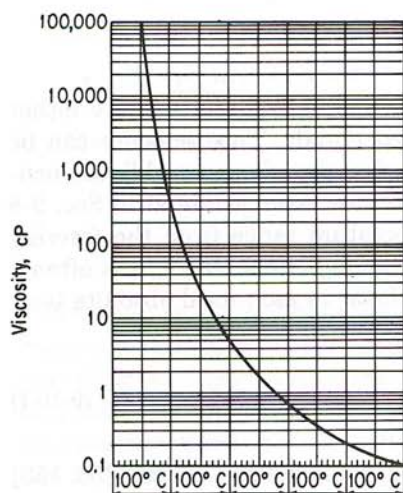
Figure 9-14 Lewis and Squires liquid viscosity-temperature correlation. *(From Ref. 131 as adapted in Ref. 77.)*

greater) may be expected. This method should not be used if the temperature is much above the normal boiling point.

Example 9-14 The viscosity of acetone at 30°C is 0.292 cP; estimate the viscosities at −90°C, −60°C, 0°C, and 60°C.

solution At −90°C, with Eq. (9-10.3),

$$\eta_L^{-0.2661} = (0.292)^{-0.2661} + \frac{-90 - 30}{233}$$

$$\eta_L = 1.7 \text{ cP}$$

For the other cases,

T, °C	η_L, cP Eq. (9-10.3)	η_L, cP Experimental	Percent error
−90	1.7	2.1	−19
−60	0.99	0.98	1
0	0.42	0.39	8
60	0.21	0.23	−9

Van Velzen et al. [212], Yaws et al. [224], and Duhne [60] have published constants to allow an estimation of liquid viscosities for most liquids for which experimental data exist. Their results have been modified slightly to yield consistent units and are shown in Table 9-8. Whenever possible, the equation forms shown in the table should be used rather than the less accurate estimation equations given in Sec. 9-11. However, the equations should *not* be used outside the recommended temperature range. A compilation similar to that of Table 9-8 is available in a paper

TABLE 9-8 Correlation of Experimental Liquid Viscosity Data[1]

Formula	Name	Eq. No.	A	B	C	D	Range, °C	η,cP at(T,°C)	Ref.
A	Argon	3	-2.851E+01	1.057E+03	2.429E-01	-8.096E-04	-189 to -124	0.25 (-185)	224
Br_2	Bromine	2	-3.112E+00	9.075E+02			-4 to 29	0.99 (19.5)	60
Cl_2	Chlorine	3	-1.768E+02	3.486E+02	-1.857E-03	7.8 E-07	-101 to 144	0.34 (25)	224
F_2	Fluorine	3	-3.629E+00	1.972E+02	-9.378E-04	-6.275E-06	-219 to -185	0.73 (-215)	224
HBr	Hydrogen bromide	3	-2.127E+01	1.996E+03	7.902E-02	-1.191E-04	-88 to 90	0.20 (25)	224
HCl	Hydrogen chloride	3	-3.488E+00	4.481E+02	7.062E-03	-3.168E-05	-110 to 50	0.068 (25)	224
HF	Hydrogen fluoride	3	-1.404E+01	1.879E+02	2.975E-02	-3.060E-05	-80 to 180	0.20 (25)	224
HI	Hydrogen iodide	3	-2.158E+01	2.337E+03	7.336E-02	-9.717E-05	-50 to 150	0.60 (25)	224
H_2	Hydrogen	3	-1.118E+01	5.786E+01	3.244E-01	-6.385E-03	-258 to -240	0.016 (-256)	224
H_2O	Water	3	-2.471E+01	4.209E+03	4.527E-02	-3.376E-05	0 to 370	0.90 (25)	224
H_3N	Ammonia	3	-1.978E+01	2.018E+03	6.173E-02	-8.317E-05	-75 to 130	0.13 (25)	224
H_2N_2	Hydrazine	3	-1.848E+01	2.991E+03	3.709E-02	-3.062E-05	2 to 370	0.90 (25)	224
H_2O_2	Hydrogen peroxide	3	-3.719E+00	1.160E+03	8.06 E-04	-2.689E-06	0 to 400	1.19 (25)	224
H_2O_4S	Sulfuric acid	2	-6.178E+00	2.736E+03			0 to 80	25.4 (20)	60
He	Helium							0.0034 (-270)	224
I_2	Iodine	3	-2.083E+00	1.195E+03	-4.566E-04	1.08 E-07	114 to 200	1.8 (150)	224
NO	Nitric oxide	3	-1.150E+01	5.487E+02	8.448E-02	-3.092E-04	-160 to -90	0.35 (-160)	224
NO_2	Nitrogen dioxide	3	-1.941E+01	2.147E+03	6.353E-02	-8.644E-05	-11 to 150	0.39 (25)	224
N_2	Nitrogen	3	-2.795E+01	8.660E+02	2.763E-01	-1.084E-03	-205 to -195	0.18 (-200)	224
N_2O	Nitrous oxide	3	1.090E+00	5.020E+01	-1.134E-02	-9.841E-06	-100 to 30	0.05 (25)	224
Ne	Neon	3	-1.929E+01	1.990E+02	5.453E-01	-6.675E-03	-248 to -229	0.137 (-247)	224
O_2	Oxygen	3	-4.771E+00	2.146E+02	1.389E-02	-6.255E-05	-218 to -120	0.47 (-210)	224
O_2S	Sulfur dioxide	3	-6.148E+00	9.365E+02	1.414E-02	-2.887E-05	-70 to 155	0.26 (25)	224
O_3S	Sulfur trioxide	3	2.894E+01	-2.277E+03	-9.392E-02	8.064E-05	16 to 210	1.60 (25)	224

TABLE 9-8 Correlation of Experimental Liquid Viscosity Data (*Continued*)

Formula a	Name	Eq. No.	A	B	C	D	Range, °C	η,cP at(T,°C)	Ref.
CCl_4	Carbon tetrachloride	3	-1.303E+01	2.290E+03	2.339E-02	-2.011E-05	-20 to 283	0.86 (25)	224
CO	Carbon monoxide	3	-5.402E+00	2.422E+02	1.062E-02	-4.522E-05	-200 to -140	0.21 (-200)	224
CO_2	Carbon dioxide	3	-3.097E+00	4.886E+01	2.381E-02	-7.840E-05	-56 to 30	0.06 (25)	224
CS_2	Carbon disulfide	2	-3.442E+00	7.138E+02			-13 to 40	0.36 (20)	60
$CHBr_3$	Bromoform	2	-3.405E+00	1.195E+03			5 to 90	1.89 (25)	212
$CHCl_3$	Chloroform	3	-4.172E+00	9.153E+02	2.70 E-03	-4.108E-06	-63 to 263	0.52 (25)	224
CH_2Br_2	Methylene bromide	2	-3.353E+00	9.876E+02			15 to 40	1.09 (15)	212
CH_2Cl_2	Methylene chloride	3	-8.061E+00	1.185E+03	1.162E-02	-1.839E-05	-97 to 240	0.41 (25)	224
CH_2O_2	Formic acid	2	-5.156E+00	1.679E+03			8 to 110	1.80 (20)	212
CH_3Cl	Methyl chloride	2	-5.073E+00	9.819E+02			0 to 130	0.18 (20)	212,173
CH_3I	Methyl iodide	2	-3.366E+00	7.741E+02			0 to 50	0.50 (20)	212
CH_3NO	Formamide	1	7.737E+23	-9.445E+02			0 to 25	3.30 (25)	224
CH_3NO_2	Nitromethane	2	-3.989E+00	1.042E+03			0 to 90	0.63 (25)	212
CH_4	Methane	3	-2.687E+01	1.150E+03	1.871E-01	-5.211E-04	-180 to -84	0.14 (-170)	224
CH_4O	Methanol	3	-3.935E+01	4.826E+03	1.091E-01	-1.127E-04	-40 to 239	0.55 (25)	224
CH_5N	Methyl amine							0.24 (0)	212
$C_2Cl_3F_3$	Trichlorotrifluoroethane	2	-4.219E+00	1.126E+03			20 to 50	0.70 (20)	212
C_2Cl_4	Tetrachloroethylene	2	-3.334E+00	9.464E+02			0 to 117	0.88 (22)	60
$C_2HF_3O_2$	Trifluoroacetic acid	2	-4.750E+00	1.348E+03			20 to 70	0.87 (20)	212
$C_2H_2Cl_4$	1,1,2,2-Tetrachloroethane	2	-4.505E+00	1.490E+03			0 to 90	1.64 (25)	212
C_2H_3N	Acetonitrile	1	3.851E+06	-2.849E+00			0 to 25	0.35 (25)	60
C_2H_4	Ethylene	3	-1.774E+01	1.078E+03	8.577E-02	-1.758E-04	-169 to 9	0.031(0)	224
$C_2H_4Br_2$	1,2-Dibromoethane	2	-3.899E+00	1.299E+03			0 to 130	1.71 (20)	212
$C_2H_4Cl_2$	1,1-Dichloroethane	2	-3.970E+00	9.493E+02			7 to 60	0.49 (19)	212
$C_2H_4Cl_2$	1,2-Dichloroethane	2	-3.926E+00	1.091E+03			0 to 100	0.83 (20)	212
$C_2H_4F_2$	1,2-Difluoroethane	2	-3.941E+00	7.352E+02			0 to 70	0.25 (20)	212

Formula	Name	Eq. No.	A	B	C	D	Range, °C	n,cP at(T, °C)	Ref.
C_2H_4O	Acetaldehyde	1	5.140E+07	-3.390E+00		-1.805E-06	0 to 20	0.22 (20)	60
C_2H_4O	Ethylene oxide	3	-3.864E+00	7.193E+02	7.44 E-04		-112 to 195	0.25 (25)	224
$C_2H_4O_2$	Methyl formate	2	-3.932E+00	8.363E+02			0 to 40	0.35 (20)	212
$C_2H_4O_2$	Acetic acid	2	-4.519E+00	1.384E+03			15 to 120	1.30 (18)	212
C_2H_5Br	Ethyl bromide	2	-3.859E+00	8.515E+02			-100 to 50	0.40 (20)	212
C_2H_5Cl	Ethyl chloride	2	-3.873E+00	7.390E+02			-20 to 50	0.27 (20)	212
C_2H_5I	Ethyl iodide	2	-3.467E+00	8.539E+02			0 to 80	0.59 (20)	212
C_2H_5NO	Acetamide	2	-5.470E+00	2.173E+03			105 to 120	1.32 (105)	60
C_2H_6	Ethane	3	-1.023E+01	6.680E+02	4.386E-02	-9.588E-05	-183 to 32	0.032(25)	224
C_2H_6O	Ethanol	3	-6.210E+00	1.614E+03	6.18 E-03	-1.132E-05	-105 to 243	1.04 (25)	224
$C_2H_6O_2$	Ethylene glycol	2	-7.811E+00	3.143E+03			20 to 110	19.9 (20)	212
C_2H_7N	Ethylamine	2						0.44 (-33)	212
$C_3H_3F_3O$	Trifluoroacetone	2	-4.684E+00	1.019E+03			8 to 25	0.33 (15)	212
$C_3H_4O_2$	Acrylic acid	1	1.510E+10	-4.089E+00			20 to 40		60
C_3H_5Br	Allyl bromide	2	-3.782E+00	8.971E+02			0 to 80	0.50 (18)	212
C_3H_5Cl	Allyl chloride	2	-4.015E+00	8.457E+02			0 to 50	0.32 (22)	212
$C_3H_5F_3O$	Trifluoro-2-propanol	2	-9.540E+00	3.115E+03			15 to 60	3.67 (15)	212
C_3H_5I	Allyl iodide	2	-3.675E+00	9.798E+02			0 to 100	0.75 (17)	212
C_3H_6	Propylene	3	-1.153E+01	9.514E+02	4.078E-02	-7.120E-05	-160 to 91	0.081(25)	224
C_3H_6	Cyclopropane	3	-3.074E+00	2.676E+02	2.55 E-04	-8.83 E-08	-127 to 124	0.12 (25)	224
$C_3H_6Br_2$	1,2-Dibromopropane	2	-3.921E+00	1.290E+03			0 to 140	1.49 (25)	212
C_3H_6O	2-Propenol	2	-5.947E+00	1.827E+03			0 to 100	1.36 (20)	212

TABLE 9-8 Correlation of Experimental Liquid Viscosity Data (Continued)

Formula	Name	Eq. No.	A	B	C	D	Range, °C	η,cP at(T,°C)	Ref.
C_3H_6O	Acetone	2	-4.033E+00	8.456E+02			-80 to 60	0.32 (25)	212
C_3H_6O	Allyl alcohol	1	3.529E+13	-5.445E+00			0 to 70	1.36 (20)	60
C_3H_6O	Propanal	2	-4.817E+00	1.153E+03			10 to 30	0.41 (20)	60
$C_3H_6O_2$	Propionic acid	2	-4.116E+00	1.232E+03			5 to 150	1.10 (20)	212
$C_3H_6O_2$	Methyl acetate	2	-4.200E+00	9.409E+02			0 to 70	0.38 (20)	212
$C_3H_6O_2$	Ethyl formate	2	-4.081E+00	9.231E+02			0 to 70	0.37 (28)	212
C_3H_7Br	Propyl bromide	2	-3.781E+00	9.102E+02			0 to 80	0.52 (19)	212
C_3H_7Br	Isopropyl bromide	2	-3.761E+00	8.922E+02			0 to 50	0.49 (20)	60
C_3H_7Cl	Propyl chloride	2	-4.014E+00	8.629E+02			0 to 50	0.35 (20)	212
C_3H_7Cl	Isopropyl chloride	2	-3.323E+00	7.052E+02			0 to 40	0.31 (22.5)	212
C_3H_7I	Propyl iodide	2	-3.715E+00	9.995E+02			0 to 100	0.73 (21)	212
C_3H_7I	Isopropyl iodide	2	-3.743E+00	9.841E+02			0 to 100	0.66 (23)	212
C_3H_7N	3-Aminopropene	2						0.37 (25)	212
$C_3H_7NO_2$	Ethyl carbamate	2	-6.578E+00	2.454E+03	-4.384E-03	5.363E-06	105 to 120	0.92 (105)	60
C_3H_7O	Propylene oxide	3	-2.717E+00	7.000E+02			-112 to 209	0.30 (25)	224
C_3H_8	Propane	3	-7.764E+00	7.219E+02	2.381E-02	-4.665E-05	-187 to 96	0.091(25)	224
C_3H_8O	n-Propanol	3	-1.228E+01	2.666E+03	2.008E-02	-2.233E-05	-72 to 260	1.94 (25)	224
C_3H_8O	Isopropanol	2	-8.114E+00	2.624E+03			0 to 90	0.98 (52)	212
$C_3H_8O_2$	Propylene glycol	2	-7.57E+00	3.233E+03			40 to 180	19.4 (40)	212
$C_3H_8O_3$	Glycerol	1	3.426E+73	-2.852E+01			0 to 30	954. (25)	60
C_3H_9N	Propyl amine							0.35 (25)	212
$C_4H_4N_2$	Succinonitrile	2	-5.183E+00	2.060E+03			59 to 83	2.76 (59)	60
C_4H_4S	Thiophene	2	-4.039E+00	1.065E+03			0 to 83	0.64 (22.5)	60
C_4H_5Cl	Chloroprene	3	-3.583E+00	7.085E+02	1.38 E-03	-1.841E-06	-130 to 260	0.38 (25)	224
C_4H_6	1,3-Butadiene	3	-6.072E+00	1.000E+03	4.46 E-03	-6.694E-06	-108 to 152	0.14 (25)	224
$C_4H_6O_3$	Acetic anhydride	2	-3.173E+00	9.054E+02			0 to 100	0.9 (18)	60

Formula	Name	Eq. No.	A	B	C	D	Range, °C	η, cP at(T,°C)	Ref.
C4H7F3O	Trifluoro-2-methylpropanol	2	-1.001E+01	3.352E+03			25 to 60	3.32 (25)	212
C4H7NO2	2 Nitro-2-butene	2	-3.855E+00	1.101E+03			30 to 70	0.81 (30)	212
C4H8	1-Butene	3	-1.063E+01	9.816E+02	3.525E-02	-5.593E-05	-140 to 146	0.17 (25)	224
C4H8	Isobutylene	3	-6.447E+00	8.135E+02	1.320E-02	-2.438E-05	-140 to 144	0.14 (25)	224
C4H8	Cyclobutane	3	-4.541E+00	6.724E+02	3.27 E-03	-3.928E-06	-90 to 190	0.19 (25)	224
C4H8Br2	1,2-Dibromo-2-methylpropane	2	-4.335E+00	1.497E+03			0 to 150	1.92 (27)	212
C4H8O	Methylethyl ketone	2	-4.213E+00	9.759E+02			0 to 80	0.42 (21)	212
C4H8O2	Butyric acid	2	-4.592E+00	1.475E+03			0 to 160	1.54 (20)	212
C4H8O2	Isobutyric acid	2	-4.355E+00	1.355E+03			4 to 150	1.38 (17)	212
C4H8O2	Methyl propionate	2	-4.173E+00	9.872E+02			0 to 80	0.41 (30)	212
C4H8O2	Ethyl acetate	2	-4.171E+00	9.841E+02			0 to 80	0.46 (20)	212
C4H8O2	Propyl formate	2	-4.238E+00	1.043E+03			0 to 90	0.51 (23)	212
C4H8O2	Isopropyl formate							0.57 (20)	212
C4H9Br	n-Butyl bromide	2	-3.805E+00	9.830E+02			0 to 100	0.65 (20)	212
C4H9Br	1-Bromo-2-methylpropane	2	-4.011E+00	1.039E+03			0 to 100	0.61 (24)	212
C4H9Cl	n-Butyl chloride	2	-4.240E+00	1.007E+03			0 to 80	0.47 (15)	60
C4H9Cl	1-Chloro-2-methylpropane							0.46 (19)	212
C4H9Cl	2-Chloro-2-methylpropane							0.54 (15)	60
C4H9I	1-Iodo-2-methylpropane	2	-3.859E+00	1.089E+03			0 to 120	0.84 (22)	212
C4H9I	Isobutyl iodide	2	-3.783E+00	1.072E+03			0 to 120	0.875(20)	60
C4H10	n-Butane	2	-3.821E+00	6.121E+02			-90 to 0	0.22 (-5)	212
C4H10	2-Methylpropane	2	-4.093E+00	6.966E+02			-80 to 0	0.27 (-20)	212
C4H10O	n-Butanol	3	-9.722E+00	2.602E+03	9.53 E-03	-9.966E-06	-60 to 289	2.61 (25)	224
C4H10O	Isobutanol	2	-8.163E+00	2.789E+03			0 to 110	3.98 (19)	212
C4H10O	2-Methylpropanol	2	-1.192E+01	3.979E+03			20 to 90	5.89 (22)	212

TABLE 9-8 Correlation of Experimental Liquid Viscosity Data (*Continued*)

Formula	Name	Eq. No.	A	B	C	D	Range, °C	n,cP at(T,°C)	Ref.
$C_4H_{10}O$	Diethyl ether	2	-4.267E+00	8.131E+02			-80 to 100	0.23 (20)	212
$C_4H_{10}O$	Methyl propyl ether	2	-4.189E+00	8.149E+02			0 to 40	0.25 (25)	212
$C_4H_{10}S$	Diethyl sulfide	2	-3.925E+00	9.156E+02			0 to 88	0.43 (25)	60
$C_4H_{11}N$	n-Butyl amine							0.68 (25)	212
$C_4H_{11}N$	Diethyl amine	2	-4.759E+00	1.091E+03			-30 to 40	0.35 (25)	212
$C_4H_{11}N$	Isobutyl amine							0.55 (25)	212
$C_5H_4O_2$	Furfural	1	3.628E+14	-5.815E+00			0 to 25	1.49 (25)	60
$C_5H_7F_3O_2$	Trifluoroacetic acid-2-propyl ester	2	-4.780E+00	1.301E+03			20 to 70	0.72 (20)	212
C_5H_8	Isoprene	3	-2.228E+00	6.357E+02	-7.32 E-03	7.665E-06	-146 to 210	0.20 (25)	224
$C_5H_9NO_2$	2-Nitro-2-pentene	2	-3.938E+00	1.147E+03			30 to 70	0.87 (30)	212
$C_5H_9NO_2$	3-Nitro-2-pentene	2	-4.070E+00	1.206E+03			30 to 70	0.93 (30)	212
C_5H_{10}	1-Pentene	2	-4.023E+00	7.029E+02			-90 to 0	0.24 (0)	212
C_5H_{10}	2-Methyl-2-butene	2	-4.115E+00	7.425E+02			0 to 40	0.21 (20)	212
C_5H_{10}	Cyclopentane	3	-6.021E+00	1.118E+03	7.28 E-03	-8.662E-06	-90 to 235	0.42 (25)	224
$C_5H_{10}O$	Diethyl ketone	2	-4.123E+00	9.798E+02			0 to 100	0.47 (19)	212
$C_5H_{10}O$	Methyl propyl ketone	2	-4.149E+00	1.008E+03			0 to 100	0.51 (18)	212
$C_5H_{10}O_2$	Valeric acid	2	-4.921E+00	1.679E+03			16 to 100	2.30 (20)	212
$C_5H_{10}O_2$	Methyl butyrate	2	-4.334E+00	1.104E+03			0 to 110	0.58 (20)	212
$C_5H_{10}O_2$	Ethyl propionate	2	-4.289E+00	1.067E+03			0 to 110	0.535 (20)	212
$C_5H_{10}O_2$	Propyl acetate	2	-4.406E+00	1.127E+03			0 to 110	0.58 (21)	212
$C_5H_{10}O_2$	n-Butyl formate	1	4.752E+10	-4.394E+00			0 to 20	0.69 (20)	60
$C_5H_{10}O_2$	Methyl isobutyrate	2	-4.222E+00	1.039E+03			0 to 100	0.47 (29)	212
$C_5H_{10}O_2$	Isopropyl acetate							0.525 (20)	212
$C_5H_{10}O_2$	Isobutyl formate							0.65 (20)	212
$C_5H_{11}Br$	n-Amyl bromide	2	-3.881E+00	1.071E+03			0 to 100	0.81 (20)	212
C_5H_{12}	n-Pentane	2	-3.958E+00	7.222E+02			-130 to 40	0.225 (25)	212

Formula	Name	Eq. No.	A	B	C	D	Range, °C	n,cP at(T,°C)	Ref.
C_5H_{12}	2-Methylbutane	2	-4.415E+00	8.458E+02			-50 to 30	0.21 (25)	212
C_5H_{12}	2,2-Dimethylpropane	2	-5.715E+00	1.248E+03			-10 to 10	0.30 (5)	212
$C_5H_{12}O$	n-Pentanol	2	-7.581E+00	2.651E+03			0 to 140	4.40 (20)	212
$C_5H_{12}O$	3-Methylbutanol	2	-7.568E+00	2.645E+03			0 to 140	3.86 (24)	212
$C_5H_{12}O$	2-Methylbutanol	2	-8.289E+00	2.900E+03			0 to 140	5.11 (20)	212
$C_5H_{12}O$	2-Methylbutanol-2	2	-1.027E+01	3.459E+03			0 to 100	5.0 (18.5)	212
$C_5H_{12}O$	Ethyl propyl ether	2	-4.315E+00	9.207E+02			0 to 70	0.32 (20)	212
$C_5H_{12}O$	Methyl isobutyl ether	2	-4.270E+00	8.972E+02			0 to 70	0.30 (21)	212
$C_5H_{13}N$	Ethyl propyl amine							0.90 (25)	212
C_6H_5Br	Bromobenzene	2	-3.869E+00	1.170E+03			0 to 150	1.17 (18)	212
C_6H_5Cl	Chlorobenzene	3	-4.573E+00	1.196E+03	1.37 E-03	-1.378E-06	-45 to 350	0.76 (25)	224
C_6H_5ClO	o-Chlorophenol	2	-6.236E+00	2.262E+03			0 to 160	4.21 (20)	212
C_6H_5ClO	m-Chlorophenol	2	-1.130E+01	4.088E+03			25 to 60	11.5 (25)	212
C_6H_5ClO	p-Chlorophenol	2	-1.169E+01	4.287E+03			45 to 60	6.15 (45)	212
C_6H_5F	Fluorobenzene	2	-4.116E+00	1.041E+03			9 to 100	0.58 (20)	212
C_6H_5I	Iodobenzene	2	-3.933E+00	1.303E+03			4 to 140	1.78 (17)	212
$C_6H_5NO_2$	Nitrobenzene	2	-4.344E+00	1.480E+03			0 to 200	2.02 (20)	212
$C_6H_5NO_3$	o-Nitrophenol	2	-5.195E+00	1.932E+03			40 to 90	2.75 (40)	212
C_6H_6	Benzene	3	4.612E+00	1.489E+02	-2.544E-02	2.222E-05	6 to 288	0.61 (25)	224
C_6H_6BrN	m-Bromoaniline	1	7.810E+18	-7.330E+02			20 to 80	6.81 (20)	60
C_6H_6BrN	o-Bromoaniline							3.19 (40)	60
C_6H_6BrN	p-Bromoaniline							1.81 (80)	60
C_6H_6ClN	2-Chloroaniline							1.65 (55)	212
C_6H_6ClN	3-Chloroaniline	2	-6.283E+00	2.242E+03			25 to 60	3.50 (25)	212

TABLE 9-8 Correlation of Experimental Liquid Viscosity Data (Continued)

Formula	Name	Eq. No.	A	B	C	D	Range, °C	n,cP at(T,°C)	Ref.
C6H6ClN	4-Chloroaniline	3	-1.851E+01	4.350E+03	2.429E-02	-1.547E-05	41 to 420	1.96 (55)	212
C6H6O	Phenol	3	3.569E+02	-3.237E+04	-1.254E+00	1.428E-03	-6 to 50	3.25 (50)	224
C6H7N	Aniline	1	4.566E+05	-2.367E+00			13 to 20	3.93 (20)	224
C6H10	Cyclohexene	2	-4.029E+00	8.062E+02			0 to 56	0.66 (20)	60
C6H10	Hexadiene-1,5	2						0.275(20)	60
C6H10	2,3-Dimethyl-1,3-butadiene	2	-4.270E+00	8.640E+02			0 to 70	0.22 (40)	212
C6H11NO2	2-Nitro-2-hexene	2	-4.123E+00	1.286E+03			30 to 70	1.14 (30)	212
C6H12	Cyclohexane	3	-4.398E+00	1.380E+03	-1.55 E-03	1.157E-06	7 to 280	0.88 (25)	224
C6H12	1-Hexene	2	-4.162E+00	8.230E+02			-55 to 70	0.25 (25)	212
C6H12	Methylcyclopentane	2	-4.170E+00	1.014E+03			-25 to 80	0.48 (25)	212
C6H12O	Methyl butyl ketone	2	-4.642E+00	1.218E+03			20 to 40	0.63 (20)	212
C6H12O	Methyl isobutyl ketone							0.58 (20)	212
C6H12O2	Caproic acid	2	-5.082E+00	1.827E+03			16 to 100	3.23 (20)	212
C6H12O2	Methyl valerate							0.71 (20)	212
C6H12O2	Ethyl butyrate	2	-4.270E+00	1.128E+03			15 to 80	0.69 (20)	212
C6H12O2	Butyl acetate	2	-4.546E+00	1.238E+03			0 to 50	0.73 (20)	212
C6H12O2	Isobutyl acetate	2	-4.546E+00	1.230E+03			20 to 100	0.72 (20)	212
C6H13Br	n-Hexyl bromide	2	-4.001E+00	1.172E+03			0 to 100	1.01 (20)	212
C6H14	n-Hexane	2	-4.034E+00	8.354E+02			-95 to 70	0.30 (25)	212
C6H14	2-Methylpentane	2	-4.247E+00	8.845E+02			0 to 70	0.285(25)	212
C6H14	2,2-Dimethylbutane	2	-4.454E+00	1.010E+03			0 to 40	0.35 (25)	212
C6H14	2,3-Dimethylbutane	2	-4.469E+00	1.023E+03			0 to 40	0.36 (25)	212
C6H14O	n-Hexanol	2	-7.651E+00	2.716E+03			20 to 60	4.37 (25)	212
C6H14O	Dipropyl ether	2	-4.391E+00	1.027E+03			0 to 100	0.40 (25)	212
C6H14O	Ethyl isobutyl ether	2	-4.404E+00	9.983E+02			0 to 80	0.37 (22)	212
C6H14O	Diisopropyl ether	2	-4.106E+00	9.216E+02			-33 to 25	0.32 (20)	212
C6H15N	Triethyl amine							0.36 (25)	60

Formula	Name	Eq. No.	A	B	C	D	Range, °C	η,cP at(T,°C)	Ref.
$C_7H_5Cl_3$	Phenyl chloroform	2	-6.567E+00	2.176E+03			10 to 20	2.55 (17)	60
$C_7H_5F_3$	Trifluorotoluene	2	-3.859E+00	9.621E+02			20 to 70	0.57 (20)	212
C_7H_5N	Benzonitrile							1.24 (25)	60
C_7H_6O	Benzaldehyde							1.39 (25)	60
$C_7H_6O_2$	Benzoic acid	2	-1.478E+01	6.027E+03			122 to 140	1.26 (130)	212
$C_7H_6O_2$	Salicylaldehyde	1	3.343E+14	-5.716E+00			10 to 40	1.67 (45)	60
$C_7H_6O_3$	Salicylic acid	2	-5.093E+00	1.750E+03			0 to 70	2.71 (20)	60
$C_7H_7NO_2$	o-Nitrotoluene	1	3.085E+13	-5.320E+00			20 to 60	2.37 (20)	212
$C_7H_7NO_2$	m-Nitrotoluene	2	-5.966E+00	2.003E+03			20 to 100	2.33 (20)	60
$C_7H_7NO_2$	p-Nitrotoluene							2.33 (20)	212
C_7H_8	Toluene	3	-5.878E+00	1.287E+03	4.575E-03	-4.499E-06	-40 to 315	0.55 (25)	224
C_7H_8O	Benzyl alcohol	2	-6.822E+00	2.505E+03			20 to 60	5.58 (20)	212
C_7H_8O	o-Cresol	2	-9.657E+00	3.531E+03			0 to 120	9.56 (20)	212
C_7H_8O	m-Cresol	2	-1.109E+01	4.111E+03			0 to 120	16.4 (20)	212
C_7H_8O	p-Cresol	2	-1.129E+01	4.207E+03			0 to 120	18.9 (20)	212
C_7H_8O	Methyl phenyl ether	2	-2.748E+00	8.953E+02			0 to 70	1.32 (20)	212
C_7H_9N	Benzyl amine	2	-4.463E+00	1.466E+03			25 to 130	1.59 (25)	212
C_7H_9N	N-Methylaniline	2	-6.333E+00	2.107E+03			0 to 80	2.30 (20)	212
C_7H_9N	2-Aminotoluene	2	-7.009E+00	2.499E+03			0 to 100	4.39 (20)	212
C_7H_9N	3-Aminotoluene	2	-6.036E+00	2.137E+03			25 to 130	3.31 (20)	212
C_7H_9N	4-Aminotoluene	2	-4.779E+00	1.701E+03			40 to 175	1.56 (55)	212
$C_7H_{11}F_3$	Trifluoromethylcyclohexane	2	-4.239E+00	1.224E+03			20 to 70	0.95 (20)	212
C_7H_{14}	1-Heptene	2	-3.961E+00	8.489E+02			0 to 100	0.34 (25)	212
C_7H_{14}	Methylcyclohexane	2	-4.480E+00	1.217E+03			-25 to 110	0.68 (25)	212
C_7H_{14}	Ethylcyclopentane	2	-4.000E+00	9.989E+02			-20 to 110	0.53 (25)	212

TABLE 9-8 Correlation of Experimental Liquid Viscosity Data *(Continued)*

Formula	Name	Eq. No.	A	B	C	D	Range, °C	n,cP at(T,°C)	Ref.
$C_7H_{14}O$	Methyl amyl ketone	2	-5.280E+00	1.973E+03			17 to 100	0.77 (25)	212
$C_7H_{14}O$	Ethyl butyl ketone	2	-4.932E+00	1.386E+03			20 to 60	0.84 (20)	212
$C_7H_{14}O$	Dipropyl ketone							0.69 (25)	212
$C_7H_{14}O_2$	Heptanoic acid							4.34 (20)	212
$C_7H_{14}O_2$	Ethyl valerate							0.84 (20)	212
$C_7H_{14}O_2$	Propyl butyrate	2	-4.604E+00	1.290E+03			20 to 60	0.83 (20)	212
$C_7H_{14}O_2$	Amyl acetate	2	-1.379E+01	4.035E+03			11 to 30	0.81 (25)	212
$C_7H_{14}O_2$	Isopropyl propionate							0.67 (25)	212
$C_7H_{14}O_2$	Isoamyl acetate	1	5.394E+10	-4.375E+00			9 to 20	0.87 (25)	60
$C_7H_{15}Br$	n-Heptyl bromide	2	-4.152E+00	1.291E+03			0 to 100	1.29 (20)	212
C_7H_{16}	n-Heptane	2	-4.325E+00	1.006E+03			-90 to 100	0.40 (25)	212
C_7H_{16}	2-Methylhexane	2	-4.270E+00	9.612E+02			0 to 100	0.36 (25)	212
$C_7H_{16}O$	n-Heptanol	2	-8.190E+00	2.964E+03			15 to 100	5.68 (25)	212
C_8H_8	Styrene	3	-2.717E+00	9.461E+02	-3.173E-03	1.683E-06	-30 to 360	0.71 (25)	224
C_8H_8O	Acetophenone	2	-4.493E+00	1.494E+03			12 to 100	1.62 (25)	212
C_8H_9O	Acetanilide	1	2.617E+16	-6.195E+00			120 to 140	2.22 (120)	60
C_8H_{10}	o-Xylene	3	-3.332E+00	1.039E+03	-1.768E-03	1.076E-06	-25 to 350	0.76 (25)	224
C_8H_{10}	m-Xylene	3	-3.820E+00	1.027E+03	-6.38 E-04	4.52 E-07	-47 to 340	0.60 (25)	224
C_8H_{10}	p-Xylene	3	-7.790E+00	1.580E+03	8.73 E-03	-6.735E-06	13 to 340	0.61 (25)	224
C_8H_{10}	Ethylbenzene	3	-6.106E+00	1.353E+03	5.112E-03	-4.552E-06	-40 to 340	0.64 (25)	224
$C_8H_{10}O$	2-Phenyl ethanol	2	-9.191E+00	3.339E+03			25 to 60	7.61 (25)	212
$C_8H_{10}O$	Ethyl phenyl ether	2	-4.869E+00	1.490E+03			0 to 90	1.25 (20)	212
$C_8H_{10}O_2$	Phenylacetic acid	2	-5.819E+00	2.471E+03			77 to 140	3.54 (77)	212

Formula	Name	Eq. No.	A	B	C	D	Range, °C	n,cP at(T,°C)	Ref.
$C_8H_{11}N$	N-Ethylaniline	2	-5.786E+00	1.943E+03			0 to 100	2.25 (20)	212
$C_8H_{11}N$	N,N-Dimethylaniline	2	-3.979E+00	1.273E+03			0 to 180	1.40 (20)	212
$C_8H_{11}NO$	o-Phenetidine	1	2.908E+33	-1.324E+01			0 to 30	6.08 (20)	60
$C_8H_{11}NO$	p-Phenetidine	1	3.346E+33	-1.314E+01			20 to 30	12.9 (20)	60
C_8H_{16}	Propylcyclopentane	2	-3.959E+00	1.046E+03			-20 to 120	0.64 (25)	212
C_8H_{16}	1-Octene	2	-4.058E+00	9.644E+02			0 to 125	0.45 (25)	212
C_8H_{16}	Ethylcyclohexane	2	-4.153E+00	1.166E+03			-25 to 125	0.785 (25)	212
$C_8H_{16}O_2$	Octanoic acid	2	-5.980E+00	2.255E+03			20 to 100	5.75 (20)	212
$C_8H_{17}Br$	n-Octyl bromide	2	-4.325E+00	1.412E+03			0 to 100	1.63 (20)	212
C_8H_{18}	n-Octane	2	-4.333E+00	1.091E+03			-55 to 125	0.51 (25)	212
$C_8H_{18}O$	n-Octanol	2	-8.166E+00	3.021E+03			15 to 100	7.21 (25)	212
$C_8H_{18}O$	Diisobutyl ether							0.75 (20)	212
$C_9H_{10}O_2$	3-Phenyl propionic acid	2	-6.488E+00	2.821E+03			50 to 140	9.8 (50)	212
$C_9H_{10}O_2$	Ethyl benzoate	2	-5.078E+00	1.719E+03			20 to 80	2.24 (20)	212
C_9H_{12}	Propylbenzene	2	-4.297E+00	1.215E+03			-25 to 160	0.80 (25)	212
C_9H_{12}	Isopropylbenzene	3	-8.292E+00	1.700E+03	1.003E-02	-7.829E-06	-20 to 360	0.74 (25)	224
C_9H_{12}	1-Methyl-4-ethylbenzene	2	-4.008E+00	1.067E+03			10 to 90	0.66 (25)	212
C_9H_{12}	1,2,4-Trimethylbenzene	2	-6.749E+00	2.010E+03			25 to 40	1.01 (25)	212
$C_9H_{12}O$	Propyl phenyl ether							1.59 (20)	212
C_9H_{18}	1-Nonene	2	-4.189E+00	1.085E+03			0 to 125	0.58 (25)	212
C_9H_{18}	Propylcyclohexane	2	-4.301E+00	1.264E+03			-25 to 125	0.93 (25)	212
C_9H_{18}	Butylcyclopentane	2	-4.159E+00	1.182E+03			-20 to 120	0.83 (25)	212
$C_9H_{18}O$	Dibutyl ketone	2	-6.002E+00	2.365E+03			20 to 100	1.28 (20)	212
$C_9H_{18}O_2$	Nonanoic acid	2	-4.531E+00	1.535E+03			0 to 100	8.08 (20)	212
$C_9H_{19}Br$	n-Nonyl bromide	2	-4.447E+00	1.210E+03			-50 to 150	2.05 (20)	212
C_9H_{20}	n-Nonane							0.67 (25)	212

TABLE 9-8 Correlation of Experimental Liquid Viscosity Data (*Continued*)

Formula	Name	Eq. No.	A	B	C	D	Range, °C	n,cP at(T,°C)	Ref.
$C_{10}H_8$	Naphthalene	3	-1.027E+01	2.517E+03	1.098E-02	-5.867E-06	81 to 475	0.78 (100)	224
$C_{10}H_{12}O_2$	Eugenol (1,3,4)	1	2.545E+36	-1.435E+01			0 to 40	9.22 (20)	60
$C_{10}H_{14}$	Butylbenzene	2	-4.386E+00	1.298E+03			-25 to 160	0.96 (25)	212
$C_{10}H_{15}N$	N,N-Diethylaniline	2	-5.577E+00	1.871E+03			0 to 100	2.18 (25)	212
$C_{10}H_{20}$	1-Decene	2	-4.297E+00	1.194E+03			0 to 125	0.75 (25)	212
$C_{10}H_{20}$	n-Butylcyclohexane	2	-4.424E+00	1.378E+03			-20 to 125	1.20 (25)	212
$C_{10}H_{20}$	Pentylcyclopentane	2	-4.309E+00	1.302E+03			-20 to 120	1.06 (25)	212
$C_{10}H_{20}O_2$	Decanoic acid	2	-5.591E+00	2.275E+03			50 to 80	4.34 (50)	212
$C_{10}H_{21}Br$	n-Decyl bromide	2	-4.704E+00	1.641E+03			0 to 100	2.55 (20)	212
$C_{10}H_{22}$	n-Decane	2	-4.460E+00	1.286E+03			-25 to 175	0.86 (25)	212
$C_{11}H_{16}$	Pentylbenzene	2	-4.658E+00	1.464E+03			-20 to 160	1.22 (25)	212
$C_{11}H_{22}$	1-Undecene	2	-4.422E+00	1.304E+03			-10 to 125	0.96 (25)	212
$C_{11}H_{22}$	n-Pentylcyclohexane	2	-4.814E+00	1.569E+03			-10 to 120	1.56 (25)	212
$C_{11}H_{22}$	Hexylcyclopentane	2	-4.463E+00	1.422E+03			-20 to 120	1.36 (25)	212
$C_{11}H_{24}$	n-Undecane	2	-4.571E+00	1.394E+03			-25 to 200	1.09 (25)	212
$C_{12}H_{10}$	Biphenyl	2	-4.572E+00	1.690E+03			70 to 450	0.95 (100)	212
$C_{12}H_{11}N$	Diphenyl amine	2	-6.629E+00	2.676E+03			55 to 130	4.66 (55)	212
$C_{12}H_{18}$	Hexylbenzene	2	-4.802E+00	1.575E+03			-20 to 160	1.52 (25)	212
$C_{12}H_{24}$	1-Dodecene	2	-4.572E+00	1.418E+03			0 to 125	1.20 (25)	212
$C_{12}H_{24}$	n-Hexylcyclohexane	2	-4.997E+00	1.697E+03			-10 to 120	1.99 (25)	212
$C_{12}H_{24}$	Heptylcyclopentane	2	-4.526E+00	1.508E+03			-20 to 120	1.72 (25)	212
$C_{12}H_{24}O_2$	Dodecanoic acid	2	-6.146E+00	2.615E+03			50 to 100	7.30 (50)	212
$C_{12}H_{26}$	n-Dodecane	2	-4.562E+00	1.454E+03			-5 to 220	1.37 (25)	212

Formula	Name	Eq. No.	A	B	C	D	Range, °C	n,cP at(T,°C)	Ref.
$C_{13}H_{10}O$	Benzophenone	2	-7.181E+00	2.886E+03			25 to 130	13.6 (25)	212
$C_{13}H_{13}N$	Benzyl phenyl amine	2	-6.415E+00	2.650E+03			55 to 130	5.4 (55)	212
$C_{13}H_{13}N$	N-Methyl diphenyl amine	2	-6.328E+00	2.428E+03			10 to 130	7.3 (20)	212
$C_{13}H_{13}N$	Benzyl amine	1	5.344E+05	-2.168E+00			33 to 130	2.18 (33)	60
$C_{13}H_{20}$	Heptylbenzene	2	-4.916E+00	1.673E+03			-20 to 160	1.88 (25)	212
$C_{13}H_{26}$	1-Tridecene	2	-4.682E+00	1.516E+03			0 to 125	1.50 (25)	212
$C_{13}H_{26}$	n-Heptylcyclohexane	2	-5.164E+00	1.814E+03			-10 to 120	2.47 (25)	212
$C_{13}H_{26}$	Octylcyclopentane	2	-4.628E+00	1.602E+03			-20 to 120	2.15 (25)	212
$C_{13}H_{28}$	n-Tridecane	2	-4.605E+00	1.529E+03			-5 to 240	1.71 (25)	212
$C_{14}H_{12}O_2$	Diethylphthalate	2	-6.589E+00	2.606E+03			25 to 60	10.1 (25)	212
$C_{14}H_{12}O_2$	Benzyl benzoate	2	-6.589E+00	2.606E+03			5 to 100	8.5 (25)	212
$C_{14}H_{14}O$	Benzyl ether	1	1.425E+22	-8.678E+00			0 to 40	5.33 (20)	60
$C_{14}H_{22}$	Octylbenzene	2	-5.190E+00	1.816E+03			-20 to 140	2.31 (25)	212
$C_{14}H_{28}$	1-Tetradecene	2	-4.778E+00	1.606E+03			0 to 125	1.83 (25)	212
$C_{14}H_{28}$	n-Octylcyclohexane	2	-5.353E+00	1.935E+03			-10 to 120	3.10 (25)	212
$C_{14}H_{28}$	Nonylcyclopentane	2	-4.732E+00	1.693E+03			-20 to 120	2.63 (25)	212
$C_{14}H_{28}O_2$	Tetradecanoic acid	2	-6.150E+00	2.705E+03			60 ro 100	7.43 (60)	212
$C_{14}H_{30}$	n-Tetradecane	2	-4.615E+00	1.588E+03			5 to 255	2.1 (25)	212
$C_{15}H_{24}$	Nonylbenzene	2	-5.352E+00	1.924E+03			-20 to 140	2.8 (25)	212
$C_{15}H_{30}$	1-Pentadecene	2	-4.898E+00	1.702E+03			0 to 125	2.24 (25)	212
$C_{15}H_{30}$	n-Nonylcyclohexane	2	-5.511E+00	2.042E+03			-10 to 120	3.80 (25)	212
$C_{15}H_{30}$	Decylcyclopentane	2	-4.825E+00	1.777E+03			-20 to 120	3.20 (25)	212
$C_{15}H_{32}$	n-Pentadecane	2	-4.648E+00	1.654E+03			10 to 280	2.56 (25)	212

TABLE 9-8 Correlation of Experimental Liquid Viscosity Data (Continued)

Formula	Name	Eq. No.	A	B	C	D	Range, °C	η,cP at(T, °C)	Ref.
$C_{16}H_{26}$	Decylbenzene	2	-5.251E+00	1.944E+03			-15 to 160	3.36 (25)	212
$C_{16}H_{32}$	1-Hexadecene	2	-4.938E+00	1.767E+03			5 to 125	2.70 (25)	212
$C_{16}H_{32}$	n-Decylcyclohexane	2	-5.630E+00	2.132E+03			0 to 120	4.60 (25)	212
$C_{16}H_{32}$	Undecylcyclopentane	2	-4.992E+00	1.882E+03			-10 to 120	3.84 (25)	212
$C_{16}H_{32}O_2$	Hexadecanoic acid	2	-6.103E+00	2.785E+03			70 to 100	7.8 (70)	212
$C_{16}H_{34}$	n-Hexadecane	2	-4.643E+00	1.700E+03			20 to 280	3.09 (25)	212
$C_{16}H_{34}O$	Cetyl alcohol							13.4 (50)	60
$C_{17}H_{28}$	Undecylbenzene	2	-5.305E+00	2.008E+03			-10 to 160	4.0 (25)	212
$C_{17}H_{34}$	1-Heptadecene	2	-4.950E+00	1.820E+03			15 to 125	3.24 (25)	212
$C_{17}H_{34}$	n-Undecylcyclohexane	2	-5.710E+00	2.206E+03			10 to 120	5.5 (25)	212
$C_{17}H_{34}$	Dodecylcyclopentane	2	-5.100E+00	1.966E+03			-5 to 120	4.56 (25)	212
$C_{17}H_{36}$	n-Heptadecane	2	-4.642E+00	1.745E+03			25 to 200	3.7 (25)	212
$C_{18}H_{14}$	o-Terphenyl	2	-5.461E+00	2.519E+03			100 to 400	4.4 (100)	212
$C_{18}H_{14}$	m-Terphenyl	2	-4.699E+00	2.167E+03			150 to 400	1.6 (150)	212
$C_{18}H_{14}$	p-Terphenyl	2	-4.549E+00	2.098E+03			250 to 400	0.60 (250)	212
$C_{18}H_{30}$	Dodecylbenzene	2	-5.285E+00	2.044E+03			0 to 160	4.78 (25)	212
$C_{18}H_{34}O_2$	Octadecenoic acid	2	-5.907E+00	2.760E+03			20 to 200	29.4 (25)	212
$C_{18}H_{36}$	1-Octadecene	2	-4.986E+00	1.879E+03			20 to 125	3.85 (25)	212
$C_{18}H_{36}$	n-Dodecylcyclohexane	2	-5.815E+00	2.285E+03			15 to 120	6.5 (25)	212
$C_{18}H_{36}$	Tridecylcyclopentane	2	-5.228E+00	2.053E+03			5 to 120	5.4 (25)	212
$C_{18}H_{36}O_2$	Octadecanoic acid	2	-7.415E+00	3.338E+03			70 to 110	7.7 (80)	212
$C_{18}H_{38}$	n-Octadecane	2	-4.649E+00	1.790E+03			30 to 300	3.88 (30)	212

Formula	Name	Eq. No.	A	B	C	D	Range, °C	n,cP at(T,°C)	Ref.
$C_{19}H_{32}$	Tridecylbenzene	2	-5.351E+00	2.108E+03			5 to 160	5.63 (25)	212
$C_{19}H_{38}$	1-Nonadecene	2	-5.044E+00	1.944E+03			25 to 125	4.56 (25)	212
$C_{19}H_{38}$	n-Tridecylcyclohexane	2	-5.904E+00	2.357E+03			20 to 120	7.67 (25)	212
$C_{19}H_{38}$	Tetradecylcyclopentane	2	-5.328E+00	2.129E+03			10 to 120	6.29 (25)	212
$C_{19}H_{40}$	n-Nonadecane	2	-4.643E+00	1.827E+03			35 to 300	4.0 (35)	212
$C_{20}H_{34}$	Tetradecylbenzene	2	-5.354E+00	2.147E+03			15 to 160	6.6 (25)	212
$C_{20}H_{40}$	1-Eicosene	2	-5.03E+00	1.982E+03			35 to 125	4.2 (35)	212
$C_{20}H_{40}$	n-Tetradecylcyclohexane	2	-5.998E+00	2.428E+03			25 to 120	9.0 (25)	212
$C_{20}H_{40}$	Pentadecylcyclopentane	2	-5.387E+00	2.189E+03			20 to 120	7.3 (25)	212
$C_{20}H_{42}$	n-Eicosane	2	-4.651E+00	1.868E+03			40 to 300	4.14 (40)	212
$C_{21}H_{36}$	Pentadecylbenzene	2	-5.416E+00	2.206E+03			20 to 160	7.72 (25)	212
$C_{21}H_{42}$	n-Pentadecylcyclohexane	2	-6.078E+00	2.493E+03			30 to 120	8.91 (30)	212
$C_{21}H_{42}$	Hexadecylcyclopentane	2	-5.459E+00	2.251E+03			25 to 120	8.44 (25)	212
$C_{22}H_{38}$	Hexadecylbenzene	2	-5.428E+00	2.245E+03			30 to 160	7.74 (30)	212
$C_{22}H_{44}$	n-Hexadecylcyclohexane	2	-6.169E+00	2.560E+03			35 to 120	8.76 (35)	212

Footnote:
1. While the literature was often not precise, it should be assumed that the state of the liquid is saturated at the prevailing pressure.

Equation numbers refer to:

Eq. (1): $n = AT^B$

Eq. (2): $\ln n = A + B/T$

Eq. (3): $\ln n = A + B/T + CT + DT^2$

with n in cP and T, T_c in kelvins

by Luckas and Lucas [139], who present constants to determine liquid viscosities for a large number of organic compounds. The correlating equations used are Eq. (9-11.2) and a modification of Eq. (9-11.9) with a switching function to change from the former to the latter at about $T_r = 0.55$. To employ Eq. (9-11.9), accurate liquid volumes are required either from experimental data or from a separate estimation method. Although the Luckas and Lucas table may be slightly more accurate than the correlations in Table 9-8, the latter have been retained because of their simplicity and the fact they require only the state variable of temperature.

Gambill [77] mentions several other approximate one-datum-point extrapolation formulas; the estimation techniques discussed in the next section may also be used by employing a single viscosity point to yield the structural constant.

In summary, from the freezing point to near the normal boiling point, Eq. (9-10.1) is a satisfactory temperature–liquid viscosity function. Two datum points are required. If only one datum point is known, a rough approximation of the viscosity at other temperatures can be obtained from Eq. (9-10.3) or Fig. 9-14. At temperatures above the normal boiling point, Eq. (9-11.9) is preferable.

Liquid viscosities above the normal boiling point are treated in Sec. 9-12.

9-11 Estimation of Low-Temperature Liquid Viscosity

Estimation methods for low-temperature liquid viscosity often employ structural-sensitive parameters which are valid only for certain homologous series or are found from group contributions. These methods usually use some variation of Eq. (9-10.1) and are limited to reduced temperatures less than about 0.75. We present two such methods in this section. We also describe a technique which employs corresponding states concepts. None of the three methods considered is particularly reliable, and we recommend that if the compound of interest is given in Table 9-8, the correlating equations presented in the table be used to estimate viscosities rather than the techniques shown below.

Orrick and Erbar method [154]

This method employs a group contribution technique to estimate A and B in Eq. (9-11.1).

$$\ln \frac{\eta_L}{\rho_L M} = A + \frac{B}{T} \tag{9-11.1}$$

where η_L = liquid viscosity, cP
    ρ_L = liquid density at 20°C, g/cm³
    M = molecular weight
    T = temperature, K

The group contributions for obtaining A and B are given in Table 9-9. For liquids that have a normal boiling point below 20°C, use the value of ρ_L at 20°C; for liquids whose freezing point is above 20°C, ρ_L at the melting point should be employed. Compounds containing nitrogen or sulfur cannot be treated. Orrick and Erbar tested this method for 188 organic liquids. The errors varied widely, but they reported an average deviation of 15 percent. This is close to the average value of 16 percent shown in Table 9-12 for a more limited test.

Example 9-15 Estimate the viscosity of liquid n-butyl alcohol at 120°C. The experimental value is 0.394 cP.

solution From Table 9-9,

$$A = -6.95 - (0.21)(4) - 3.00 = -10.79$$
$$B = 275 + (99)(4) + 1600 = 2271$$

From Appendix A, at 20°C, $\rho_L = 0.809$ g/cm³ and $M = 74.12$. Then, with Eq. (9-11.1),

$$\ln \frac{\eta_L}{(0.809)(74.12)} = -10.79 + \frac{2271}{T}$$

At $T = 120°C = 393$ K, $\eta_L = 0.399$ cP

$$\text{Error} = \frac{0.399 - 0.394}{0.394} \times 100 = 1.3\%$$

Van Velzen, Cardozo, and Langenkamp method

In an unusually detailed study of the effect of structure on liquid viscosities, van Velzen et al. [211, 212] proposed a modification of Eq. (9-10.1),

$$\log \eta_L = B(T^{-1} - T_0^{-1}) \tag{9-11.2}$$

where η_L = liquid viscosity, cP
    T = temperature, K

and B and T_0 are related to structure. To determine these parameters, one must first find the *equivalent chain length N^**, where

$$N^* = N + \Sigma \, \Delta N_i \tag{9-11.3}$$

N is the actual number of carbon atoms in the molecule, and ΔN represents structural contributions from Table 9-10. If the structural or functional group ΔN_i appears n_i times in the molecule, $n_i \, \Delta N_i$ corrections must

TABLE 9-9 Orrick and Erbar Group Contributions for A and B in Eq. (9-11.1) [154]

Group	A	B
Carbon atoms†	$-(6.95+0.21n)$	$275+99n$
R—C—R with R above and R below	-0.15	35
R—C—R with R above and R below	-1.20	400
Double bond	0.24	-90
Five-membered ring	0.10	32
Six-membered ring	-0.45	250
Aromatic ring	0	20
Ortho substitution	-0.12	100
Meta substitution	0.05	-34
Para substitution	-0.01	-5
Chlorine	-0.61	220
Bromine	-1.25	365
Iodine	-1.75	400
—OH	-3.00	1600
—COO—	-1.00	420
—O—	-0.38	140
—C=O	-0.50	350
—COOH	-0.90	770

†n = number, not including those in groups shown above.

be added. In the tabulation of ΔN_i contributions, some entries are to be used every time the functional group appears; other entries represent additional *corrections* to be used to modify the basic group contribution. A few examples given below illustrate the technique of calculating N^*.

Example 9-16 Calculate N^* for benzophenone, chloroform, N-methyldiphenyl-amine, N,N-diethylaniline, allyl alcohol, and m-nitrotoluene.

solution For benzophenone, $C_6H_5COC_6H_5$, $N = 13$ (number of carbon atoms). There is a ΔN_i contribution for ketones, that is, $3.265 - 0.122N = 3.265 - (0.122)(13) = 1.68$. Also, there is a *correction* for aromatic ketones of 2.70 for each aromatic ring; thus,

$$N^* = 13 + 1.68 + (2)(2.70) = 20.08$$

For chloroform, $N = 1$. Each of the three chlorine atoms has a ΔN_i contribution of 3.21. Also, there is a *correction* term for the $C(Cl)_x$ structure of $1.91 - 1.459x$, where, in this case, $x = 3$. Thus,

$$N^* = 1 + (3)(3.21) + 1.91 - (3)(1.459) = 8.16$$

For N-methyldiphenylamine, $(C_6H_5)_2N(CH_3)$, $N = 13$. This is a tertiary amine, so that $\Delta N_i = 3.27$. Also, there is a *correction* for each of the aromatic groups (see note f of Table 9-10) of 0.6. Then

$$N^* = 13 + 3.27 + (2)(0.6) = 17.47$$

For N,N-diethylaniline, $(C_6H_5)N(C_2H_5)_2$, $N = 10$. Again, a tertiary amine contribution of 3.27 is required, but only one aromatic group is present with a correction of 0.6:

$$N^* = 10 + 3.27 + 0.6 = 13.87$$

For allyl alcohol, $CH_2{=}CHCH_2OH$, $N = 3$. As a primary alcohol, there is a ΔN_i of $10.606 - 0.276N = 10.606 - (3)(0.276) = 9.778$. In addition, as an alkene, another ΔN_i of $-0.152 - 0.042N = -0.152 - (3)(0.042) = -0.278$ is necessary. Thus,

$$N^* = 3 + 9.778 - 0.278 = 12.50$$

Finally, for m-nitrotoluene, $C_6H_4NO_2(CH_3)$, $N = 7$. The ΔN_i for the aromatic nitro compound is $7.812 - 0.236N = 7.812 - (7)(0.236) = 6.16$. There is no contribution for an alkyl benzene. For the meta correction (see note a of Table 9-10), $\Delta N_i = 0.11$. Thus,

$$N^* = 7 + 6.16 + 0.11 = 13.27$$

The value of N^* is then used to determine the constants B and T_0 which appear in Eq. (9-11.2). For T_0,

$$T_0 = \begin{cases} 28.86 + 37.439N^* - 1.3547(N^*)^2 + 0.02076(N^*)^3 & N^* < 20 \quad (9\text{-}11.4) \\ 8.164N^* + 238.59 & N^* > 20 \quad (9\text{-}11.5) \end{cases}$$

TABLE 9-10 Van Velzen, Cardozo, and Langenkamp Contributions for Liquid Viscosity [211]

Structures or functional group	ΔN_i	ΔB_i	Example Compound	N^*	B	T_0	Remarks
n-Alkanes	0	0	n-Hexane	6.00	377.86	209.21	
Isoalkanes	$1.389 - 0.298N$	15.51	2-Methylbutane	5.20	351.95	189.83	
Saturated hydrocarbons with two methyl groups in iso position	$2.319 - 0.298N$	15.51	2,3-Dimethylbutane	6.89	437.37	229.29	
n-Alkenes	$-0.152 - 0.042N$	$-44.94 + 5.410N^*$	1-Octene	7.51	446.89	242.41	
n-Alkadienes	$-0.304 - 0.084N$	$-44.94 + 5.410N^*$	1,3-Butadiene	3.36	211.21	140.15	
Isoalkenes	$1.237 - 0.280N$	$-36.01 + 5.410N^*$	2-Methyl-2-butene	4.84	307.40	180.68	
Isoalkadienes	$1.085 - 0.322N$	$-36.01 + 5.410N^*$	2-Methyl-1,3-butadiene	4.48	285.89	171.26	
Hydrocarbon with one double bond and two methyl groups in iso position	$2.626 - 0.518N$	$-36.01 + 5.410N^*$	2,3-Dimethyl-1-butene	5.52	347.07	197.74	For any additional CH_3 groups in iso position, increase ΔN by $1.389 - 0.238N$
Hydrocarbon with two double bonds and two methyl groups in iso position	$2.474 - 0.560N$	$-36.01 + 5.410N^*$	2,3-Dimethyl-1,3-butadiene	5.11	323.30	187.57	For any additional CH_3 groups in iso position, increase ΔN by $1.389 - 0.238N$
Cyclopentanes	$0.205 + 0.069N$	$-45.96 + 2.224N^*$	n-Butylcyclopentane	9.83	527.3	285.7	$N < 16$; not recommended for $N = 5, 6$
	$3.971 - 0.172N$	$-339.67 + 23.135N^*$	Tridecylcyclopentane	18.87	889.40	392.45	$N \geq 16$
Cyclohexanes	1.48	$-272.85 + 25.041N^*$	Ethylcyclohexane	9.48	501.80	279.72	$N < 17$; not recommended for $N = 6, 7$
	$6.517 - 0.311N$	$-272.85 + 25.041N^*$	Dodecylcyclohexane	18.92	994.10	392.87	$N \geq 17$
Alkyl benzenes	0.60	$-140.04 + 13.869N^*$	o-Xylene	9.11	563.09	273.20	$N < 16$; not recommended for $N = 6, 7$[a,e,f]
	$3.055 - 0.161N$	$-140.04 + 13.869N^*$					$N \geq 16$[a,e,f]
Polyphenyls	$-5.340 + 0.815N$	$-188.40 + 9.558N^*$	m-Terphenyl	27.44	1008.7	462.58	[a]
Alcohols: Primary	$10.606 - 0.276N$	$-589.44 + 70.519N^*$	1-Pentanol	14.23	1113.0	347.12	[b]
Secondary	$11.200 - 0.605N$	497.58	Isopropyl alcohol	12.38	1141.35	324.12	[b]
Tertiary	$11.200 - 0.605N$	928.83	2-Methyl butanol-2	13.42	1699.1	337.49	[b]
Diols (correction)	See remarks	557.77	Propylene glycol	22.66	1399.71	423.55	For ΔN, use alcohol contributions and add $N - 2.50$
Phenols (correction)	$16.17 - N$	213.68					[a,c,d]
—OH on side chain to aromatic ring (correction)	-0.16	213.68					
Acids	$6.795 + 0.365N$	$-249.12 + 22.449N^*$	n-Butyric acid	12.25	665.40	322.96	$N < 11$, not recommended for $N = 1, 2$
	10.71	$-249.12 + 22.449N^*$					$N \geq 11$

Compound type		Example				Remarks
Iso acids	See remarks	$-249.12 + 22.449N$*	Isobutyric acid	12.01	652.02	319.06	Calculate ΔB as for straight-chain acid; calculate ΔN for straight-chain acid but reduce ΔN by 0.24 for each methyl group in iso position
Acids with aromatic nucleus in structure (correction)	4.81	$-188.40 + 9.558N$*	Phenylacetic acid	22.52	1123.29	422.41	
Esters	$4.337 - 0.230N$	$-149.13 + 18.695N$*	Ethyl valerate	9.73	580.16	284.01	If hydrocarbon groups have iso configuration, see footnote e. Add to values of ΔN, ΔB calculated for ester
Esters with aromatic nucleus in structure (correction)	$-1.174 + 0.376N$	$-140.04 + 13.869N$*	Benzyl benzoate	19.21	1133.17	395.31	
Ketones	$3.265 - 0.122N$	$-117.21 + 15.781N$*	Methyl n-butyl ketone	8.53	514.53	262.53	If hydrocarbon groups have iso configuration, see footnote e. Add to values of ΔN, ΔB calculated for ketone
Ketones with aromatic nucleus in structure (correction)	2.70	$-760.65 + 50.478N$*	Acetophenone	12.99	645.92	322.10	
Ethers	$0.298 + 0.209N$	$-9.39 + 2.848N$*	Ethyl hexyl ether	9.97	575.96	288.04	If hydrocarbon groups have iso configuration, see footnote e
Aromatic ethers	$11.5 - N$	$-140.04 + 13.869N$*	Propyl phenyl ether	11.5	656.83	311.82	^{c}The ΔN value is not a correction to regular ether value, but the ΔB value is a correction to regular ether
Amines:							
Primary	$3.581 + 0.325N$	$25.39 + 8.744N$*	Propylamine	7.56	545.01	243.44	If hydrocarbon groups have iso configuration, see footnote e
Primary amine in side chain of aromatic compound (correction)	-0.16	0	Benzylamine	12.70	790.47	328.36	Corrections to be added to amine calculation^e
Secondary	$1.390 + 0.461N$	$25.39 + 8.744N$*	Ethylpropylamine	8.69	605.44	265.53	If hydrocarbon groups have iso configuration, see footnote e
Tertiary	3.27	$25.39 + 8.744N$*.		⋯	⋯	⋯	If hydrocarbon groups have iso configuration, see footnote e
Primary amines with NH$_2$ group on aromatic nucleus	$15.04 - N$	0	m-Toluidine	15.04	904.08	356.13	^{a} The ΔN value is not a correction to regular amine value; to find ΔB use primary amine value
Secondary or tertiary amine with at least one aromatic group attached to amino nitrogen			Benzylphenylamine	21.58	1041.18	414.74	
Nitro compounds:							
1-nitro	$7.812 - 0.236N$	$-213.14 + 18.330N$*	Nitromethane	8.57	442.82	263.28	Note alkene contribution is necessary
2-nitro	5.84	$-213.14 + 18.330N$*	2-Nitro-2-pentene	10.48	567.43	296.33	
3-nitro	5.56	$-338.01 + 25.086N$*					
4-nitro; 5-nitro	5.56	$-338.01 + 25.086N$*					
Aromatic nitro-compounds	$7.812 - 0.236N$	$-213.14 + 18.330N$*	Nitrobenzene	13.00	728.79	332.23	For aromatic correction see footnote f

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TABLE 9-10 Van Velzen, Cardozo, and Langenkamp Contributions for Liquid Viscosity (*Continued*)

Structures or functional group	ΔN_i	ΔB_i	Example Compound	N^*	B	T_0	Remarks
Halogenated compounds:							
Fluoride	1.43	5.75					
Chloride	3.21	-17.03	Ethyl chloride	5.21	319.94	190.08	√
Bromide	4.39	$-101.97 + 5.954N^*$	1-Bromo-2-methyl propane	8.15	435.85	255.24	√
Iodide	5.76	-85.92	Iodobenzene	12.36	589.18	323.85	√
Special configurations (corrections):							
$C(Cl)_x$	$1.91 - 1.459x$	-26.38					
—CCl—CCl—	0.96	0					
—C$(Br)_x$—	0.50	$81.34 - 86.850x$					
—CBr—CBr—	1.60	-57.73					
CF_3, in alcohols	-3.93	341.68					
In other compounds	-3.93	25.55					
Aldehydes	3.38	$146.45 - 25.11N^*$	Propionaldehyde	6.38	383.16	217.97	
Aldehydes with an aromatic nucleus in structure (correction)	2.70	$-760.65 + 50.478N^*$	Benzaldehyde	13.08	391.19	333.25	
Anhydrides	$7.97 - 0.50N$	-33.50	Propionic anhydride	10.79	554.87	301.19	
Anhydrides with an aromatic nucleus in structure (correction)	2.70	$-760.65 + 50.478N^*$					
Amides	$13.12 + 1.49N$	$524.63 - 20.72N^*$	Acetamide	18.10	931.07	385.79	
Amides with an aromatic nucleus in structure (correction)	2.70	$-760.65 + 50.478N^*$					

a For substitutions on an aromatic nucleus in more than one position, additional corrections are required:

Ortho:	$\Delta N = 0.51$	$\Delta B = \begin{cases} -571.94 & \text{with —OH} \\ 54.84 & \text{without —OH} \end{cases}$
Meta:	$\Delta N = 0.11$	$\Delta B = 27.25$
Para:	$\Delta N = -0.04$	$\Delta B = -17.57$

b For alcohols, if there is a methyl group in the iso position, increase ΔN by 0.24 and ΔB by 94.23.

c If the compound has an aromatic —OH or —NH$_2$, or if it is an aromatic ether, use ΔN contribution in table but neglect other substituents on the ring such as halogen, CH$_3$, NO$_2$, etc. For the calculation of ΔB, however, such substituents must be taken into account.

d For aromatic alcohols and compounds with an —OH on a side chain, the alcohol contribution (primary, etc.) must be included. For example, o-chlorophenol:

$$\Delta B = \Delta B \text{ (primary alcohol)} + \Delta B \text{ (chlorine)} + \Delta B \text{ (phenol)} + \Delta B \text{ (ortho correction[a])}$$

With $N^* = 16.17$[e]:

$$\Delta B = (-589.44 + 70.519 \times 16.17) + (-17.03) + (213.68) + (-571.94) = 175.56$$
$$B_a = 745.94 \qquad B = B_a + \Delta B = 921.50$$

2-Phenylethanol:

$$N = 8 \qquad \Delta N = \Delta N \text{ (primary alcohol)} + \Delta N \text{ (correction)} = [10.606 - (0.276)(8)] + (-0.16) = 8.24$$
$$N^* = N + \Delta N = 8 + 8.24 = 16.24$$
$$\Delta B = \Delta B \text{ (primary alcohol)} + \Delta B \text{ (correction)} = [-589.44 + (70.519)(16.24)] + 213.68 = 769.47$$
$$B_a = 747.43 \qquad B = B_a + \Delta B = 1516.9$$

e For esters, alkylbenzenes, halogenated hydrocarbons, and ketones, if the hydrocarbon chain has a methyl group in an iso position, decrease ΔN by 0.24 and increase ΔB by 8.93 for each such grouping. For ethers and amines, decrease ΔN by 0.50 and increase ΔB by 8.93 for each iso group.

f For alkylbenzenes, nitrobenzenes, halogenated benzenes, and for secondary or tertiary amines where at least one aromatic group is connected to an amino nitrogen, add the following corrections for each aromatic nucleus. If $N < 16$, increase ΔN by 0.60; if $N \geq 16$, increase ΔN by $3.055 - 0.161N$ for each aromatic group. For any N, increase ΔB by $(-140.04 + 13.869N^*)$.

For B,

$$B = B_A + \Sigma \, \Delta B_i \qquad (9\text{-}11.6)$$

where

$$B_A = \begin{cases} 24.79 + 66.885N^* - 1.3173(N^*)^2 - 0.00377(N^*)^3 & N^* < 20 \quad (9\text{-}11.7) \\ 530.59 + 13.740N^* & N^* > 20 \quad (9\text{-}11.8) \end{cases}$$

and $\Sigma \, \Delta B_i$ can be determined by summing contributions as shown in Table 9-10. Even though a functional group may appear more than once in a compound, the ΔB_i contribution is applied only a single time.

The B and T_0 values found for any specific compound are then used in Eq. (9-11.2) and the liquid viscosity is determined. The units of η_L and T are centipoises and kelvins.

Example 9-17   Obtain the constants B and T_0 for benzophenone and estimate the liquid viscosity at at 25, 55, 95, and 120°C. Experimental values are 13.61, 4.67, 1.74, and 1.38 cP.

solution N^* was calculated in Example 9-16 as 20.08. To determine T_0, since $N^* > 20$, Eq. (9-11.5) must be used.

$$T_0 = (8.164)(20.08) + 238.59 = 402.52$$

For B, first B_A is determined from Eq. (9-11.8),

$$B_A = 530.59 + (13.740)(20.08) = 806.49$$

The ΔB_i corrections are

$$\Delta B \text{ (ketone)} = -117.21 + (15.781)(20.08) = 199.67$$
$$\Delta B \text{ (aromatic ketone correction)} = -760.65 + (50.478)(20.08) = 252.95$$
$$B = 806.49 + 199.67 + 252.95 = 1259.11$$

Then, from Eq. (9-11.2),

$$\log \eta_L = 1259.11[T^{-1} - (402.52)^{-1}]$$

T, °C	η_L, cP Calc.	Exp.	% Error
25	12.44	13.61	−8.7
55	5.11	4.67	9.4
95	1.96	1.74	12
120	1.19	1.38	−14

Van Velzen et al. tested their method on 314 different liquids with nearly 4500 datum points, and a careful statistical evaluation was made. Large errors were often noted for the first members of a homologous series. This point is significant because, in the comparison of calculated and experimental liquid viscosities in Table 9-11, many of the test com-

pounds shown are first members of a series. This reflects unfairly on the van Velzen et al. method.

Some care must be used in selecting appropriate ΔN_i and ΔB_i contributions. A Euratom report [212] is very helpful in illustrating the rules for complex compounds.

Przezdziecki and Sridhar method [160]

In this technique the authors propose using the Hildebrand-modified Batschinski equation [15, 99, 217].

$$\eta_L = \frac{V_0}{E(V - V_0)} \tag{9-11.9}$$

where η_L = liquid viscosity, cP
$\qquad V$ = liquid molar volume, cm^3/mol

and the parameters E and V_0 are defined below.

$$E = -1.12 + \frac{V_c}{12.94 + 0.10M - 0.23P_c + 0.0424T_f - 11.58(T_f/T_c)} \tag{9-11.10}$$

$$V_0 = 0.0085\omega T_c - 2.02 + \frac{V_m}{0.342(T_f/T_c) + 0.894} \tag{9-11.11}$$

where T_c = critical temperature, K
$\qquad P_c$ = critical pressure, bar
$\qquad V_c$ = critical volume, cm^3/mol
$\qquad M$ = molecular weight, g/mol
$\qquad T_f$ = freezing point, K
$\qquad \omega$ = acentric factor
$\qquad V_m$ = liquid molar volume at T_f, cm^3/mol

Thus, to use Eq. (9-11.9), one must have values for T_c, P_c, V_c, T_f, ω, and V_m in addition to the liquid molar volume V at the temperature of interest. Rarely does one have data for V_m or even V, and even if data are available, the authors recommend that these two liquid volumes be estimated from T_f and T by the Gunn-Yamada method [89]. In this procedure, one accurate value of V is required in the temperature range of applicability of Eq. (9-11.9). We define this datum point as V^R at T^R; then at any other temperature T,

$$V(T) = \frac{f(T)}{f(T^R)} V^R \tag{9-11.12}$$

where $\quad f(T) = H_1(1 - \omega H_2) \tag{9-11.13}$

$$H_1 = 0.33593 - 0.33953T_r + 1.51941T_r^2 - 2.02512T_r^3$$
$$+ 1.11422T_r^4 \tag{9-11.14}$$

$$H_2 = 0.29607 - 0.09045T_r - 0.04842T_r^2 \tag{9-11.15}$$

TABLE 9-11 Comparison of Calculated and Experimental Viscosities of Liquids

Compound	T, K	η_L, (exp.) cP‡	Orrick and Erbar	Van Velzen, Cardozo, and Langenkamp	Przezdziecki and Sridhar
			Percent error† in liquid viscosity calculated by the method of		
Acetone	183	2.075	−25	−20	−11
	213	0.982	−15	−9.0	−13
	273	0.389	−8.3	0.1	−2.3
	303	0.292	−9.4	−0.2	−1.2
	333	0.226	−8.3	1.6	0.2
Acetic acid	283	1.45	−22	−34	8.6
	313	0.901	−15	−28	0
	353	0.561	−9.5	−24	−1.3
	383	0.416	−5.3	−21	0.3
Aniline	263	13.4	—	−52	—
	293	4.38	—	−23	—
	333	1.52	—	−2.8	−49
	393	0.658	—	−11	−33
Benzene	278	0.826	−45	−42	1.1
	313	0.492	−35	−30	7.3
	353	0.318	−26	−20	12
	393	0.219	−46	−8.5	18
	433	0.156	−7.1	5.8	23
	463	0.121	5.1	20	28
n-Butane	183	0.63	−14	−7.2	−9.0
	213	0.403	−20	−9.8	−8.9
	273	0.210	−23	8.8	−5.8
1-Butene	163	0.79	−22	−6.1	−13
	193	0.45	−20	0	−9.6
	233	0.26	−18	8.7	−3.3
n-Butyl alcohol	273	5.14	−2.1	5.6	—
	313	1.77	−1.6	0	—
	353	0.762	0.5	−2.3	—
	393	0.394	−1.4	−5.3	—
Carbon tetrachloride	273	1.369	20	−10	−24
	303	0.856	22	−6.1	−15
	343	0.534	20	−4.3	−6.7
	373	0.404	19	−4.0	−2.8
Chlorobenzene	273	1.054	1.4	15	−8.3
	313	0.639	−0.6	7.0	−7.0
	353	0.441	−0.9	0.2	−5.2
	393	0.326	−5.1	−5.0	−3.8
Chloroform	273	0.700	40	11	−11
	303	0.502	34	7.0	−8.1
	333	0.390	27	2.1	−7.9
Cyclohexane	278	1.300	−51	−51	−38
	333	0.528	−38	−27	−22
Cyclopentane	293	0.439	−32	−32	−33
	323	0.323	−28	−26	−29
2,2-Dimethylpropane	258	0.431	−3.5	7.2	20
	283	0.281	−0.8	20	30

Compound	T, K	η_L, (exp.) cP‡	Percent error† in liquid viscosity calculated by the method of		
			Orrick and Erbar	Van Velzen, Cardozo, and Langenkamp	Przezdziecki and Sridhar
Ethane	98	0.985	30	2.6	−24
	153	0.257	−12	8.2	−14
	188	0.162	−22	12	−13
Ethylene chloride	273	1.123	−43	−4.0	—
	313	0.644	−35	−4.0	—
	353	0.417	−27	−3.5	—
Ethyl alcohol	273	1.770	27	69	—
	313	0.826	3.5	38	—
	348	0.465	−5.4	27	—
Ethyl acetate	293	0.458	−4.2	3.1	−16
	353	0.246	0.4	7.2	−5.3
	413	0.153	7.4	14	−1.8
	463	0.0998	27	34	4.8
Ethylbenzene	253	1.24	−2.9	−3.8	−33
	313	0.535	−1.2	−3.3	−23
	373	0.308	−1.7	−4.7	−16
	413	0.231	−1.2	−4.6	−13
Ethyl bromide	293	0.395	27	2.9	−23
	333	0.269	32	10	−17
	373	0.199	36	16	−16
Ethylene	103	0.70	−25	4.0	−25
	133	0.31	−27	40	−17
	173	0.15	−22	—	−6.4
Ethyl ether	273	0.289	0	−4.7	0
	293	0.236	0	−3.9	2.2
	333	0.167	2.0	−1.2	4.0
	373	0.118	11	8.8	7.4
Ethyl formate	273	0.507	−18	−3.3	−16
	303	0.362	−17	−1.8	−11
	328	0.288	−16	−1.2	−9.6
n-Heptane	183	3.77	−21	18	−1.7
	233	0.965	−0.5	0.8	−27
	293	0.418	−1.9	−1.8	−21
	373	0.209	−3.3	−4.4	−17
n-Hexane	213	0.888	2.9	4.2	−8.3
	273	0.381	−2.4	−0.9	−8.2
	343	0.205	−4.9	−3.8	−7.1
Isobutane	193	0.628	−23	−3.5	−37
	233	0.343	−25	−6.4	−29
	263	0.239	−24	−5.4	−23
Isopropyl alcohol	283	3.319	−24	−2.8	—
	303	1.811	−15	−3.4	—
	323	1.062	−10	−3.6	—
Methane	88	0.226	60	—	−11
	113	0.115	23	—	−4.3

(Continued)

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TABLE 9-11   **Comparison of Calculated and Experimental Viscosities of Liquids** (*Continued*)

			Percent error† in liquid viscosity calculated by the method of		
Compound	T, K	η_L, (exp.) cP‡	Orrick and Erbar	Van Velzen, Cardozo, and Langenkamp	Przezdziecki and Sridhar
2-Methylbutane	223	0.55	−13	−4.0	−30
	253	0.353	−12	−2.7	−21
	303	0.205	−10	−1.1	−12
n-Pentane	153	2.35	−1.0	−1.7	11
	193	0.791	3.8	5.5	−7.0
	233	0.428	−3.3	0.6	−6.0
	273	0.279	−8.2	−3.6	−4.7
	303	0.216	−11	−5.2	−4.9
Phenol	323	3.020	0	22	−50
	373	0.783	37	11	−5.4
Propane	133	0.984	−1.5	−8.4	−23
	193	0.327	−22	−12	−19
	233	0.205	−25	−9.7	−16
n-Propyl alcohol	283	2.897	−9.1	4.1	—
	313	1.400	−9.8	1.4	—
	373	0.443	−6.5	2.0	—
Toluene	253	1.07	−19	−19	−33
	293	0.587	−13	−29	−24
	333	0.380	−10	−8.7	−16
	383	0.249	−6.8	−4.6	−10
o-Xylene	273	1.108	3.1	−9.7	−5.5
	313	0.625	5.0	−13	−4.8
	373	0.345	3.7	−1.1	−0.3
	413	0.254	3.6	−21	1.9
m-Xylene	273	0.808	1.1	9.9	1.9
	313	0.492	1.4	3.9	1.8
	353	0.340	0.3	−1.9	2.9
	413	0.218	1.4	−5.8	4.6

†[(calc. − exp.)/exp.] × 100.
‡Refs. 5 and 129.

Equation (9-11.9) was employed with Eqs. (9-11.10) to (9-11.15) to estimate liquid viscosities for the compounds in Table 9-11. The values of T_c, P_c, V_c, T_f, and ω were obtained from Appendix A. The reference volume for each compound was calculated from the liquid density datum value given in Appendix A. Large errors were noted for alcohols, and those results are not included in the table. For other compounds, the errors varied widely and, except for a few materials, the technique underestimated the liquid viscosity. Larger errors were normally noted at low temperatures, but that might have been expected from the form of Eq. (9-11.9). That is, because V_0 is of the order of the volume at the freezing point and $\eta_L \propto (V - V_0)^{-1}$, the estimated value of η_L becomes exceedingly sensitive

to the choice of V. This problem was emphasized by Luckas and Lucas [139], who suggest that Eq. (9-11.9) should not be used below T_r values of about 0.55.

Example 9-18 Use the Przezdziecki and Sridhar correlation to estimate the liquid viscosity of toluene at 383 K. The experimental value is 0.249 cP [215].

solution From Appendix A, for toluene

T_c = 591.8 K

P_c = 41.0 bar

V_c = 316 cm³/mol

T_f = 178 K

M = 92.14 g/mol

ω = 0.263

ρ_L = 0.867 g/cm³ at 293 K

Thus, V^R = 92.14/0.867 = 106.3 cm³/mol at T^R = 293 K. With Eqs. (9-11.12) to (9-11.15),

$$T = T^R; \quad T_r^R = \frac{293}{591.8} = 0.495$$

$$H_1(T_r^R) = 0.33593 - (0.33953)(0.495) + (1.51941)(0.495)^2$$
$$- (2.02512)(0.495)^3 + (1.11422)(0.495)^4 = 0.361$$

$$H_2(T_r^R) = 0.29607 - (0.09045)(0.495) - (0.04842)(0.495)^2 = 0.239$$

$$f(T^R) = 0.361[1 - (0.263)(0.239)] = 0.338$$

Similarly,

	T, K	T_r	H_1	H_2	$f(T)$
T_f	178	0.301	0.325	0.265	0.302
T	383	0.647	0.399	0.206	0.377

Then $\quad V_m = \dfrac{0.302}{0.338}(106.3) = 95.0$ cm³/mol

$\quad\quad\quad\quad V = \dfrac{0.377}{0.338}(106.3) = 118.6$ cm³/mol

With Eqs. (9-11.10) and (9-11.11),

$$E = -1.12 + 316/[12.94 + (0.10)(92.14) - (0.23)(41.0)$$
$$+ (0.0424)(178) - (11.58)(178/591.8)]$$

$$= 17.70$$

$$V_0 = (0.0085)(0.263)(591.8) - 2.02 + \frac{95.0}{[(0.342)(178/591.8) + 0.894]}$$

$$= 94.6 \text{ cm}^3/\text{mol}$$

Then, with Eq. (9-11.9)

$$\eta_L = \frac{94.6}{17.70(118.6 - 94.6)} = 0.223 \text{ cP}$$

$$\text{Error} = \frac{0.223 - 0.249}{0.249} \times 100 = -10\%$$

In this case Vargaftik [215] gives the value of the liquid molar volume at 383 K as 118.2 cm³/mol. Using this number rather than the estimated value of 118.6 cm³/mol leads to an error in the viscosity of -9%.

Other correlations

Many viscosity-correlating methods have been proposed, but few are predictive in nature. Of those that are, group contribution approaches have been used [41, 149, 181, 182, 202]. Most other estimation methods relate the liquid viscosity to other physical properties (assumed known) and, in addition, require one or more constants to be determined from experimental data. Luckas and Lucas [139] recently proposed an alternative group contribution method to estimate liquid viscosities. The method is promising, but, at present, only a few group values are available. Other recent correlations are given in Refs. 106, 112, 113, 157, 203, 204, and the earlier literature was reviewed in the third edition of this book.

Recommendations for estimating low-temperature liquid viscosities

Three estimation methods have been discussed. In Table 9-11 calculated liquid viscosities are compared with experimental values for 35 different liquids (usually of simple structure). Large errors may result, as illustrated for all methods. The method of van Velzen et al. is *not* recommended for first members of a homologous series, and the method of Przezdziecki and Sridhar should not be used for alcohols.

The method of van Velzen et al. assumes that log η_L is linear in T^{-1}, whereas the Orrick and Erbar method is slightly modified to include the liquid density. Neither is reliable for highly branched structures (van Velzen et al. can treat only iso compounds) or for inorganic liquids or sulfur compounds. Both are limited to a temperature range from somewhat above the freezing point to about $T_r \approx 0.75$. Przezdziecki and Sridhar's method employs the Hildebrand equation, which necessitates knowledge of liquid volumes.

It is recommended that, in general, the method of van Velzen, Cardozo, and Langenkamp be used to estimate low-temperature liquid viscosities except for first members of a homologous series. Errors vary widely, but

as judged from extensive testing [211], errors should be less than 10 to 15 percent in most instances.

9-12 Estimation of Liquid Viscosity at High Temperatures

Low-temperature viscosity correlations as covered in Sec. 9-10 usually assume that $\ln \eta_L$ is a linear function of reciprocal absolute temperature. Above a reduced temperature of about 0.7, this relation is no longer valid, as illustrated in Fig. 9-10. In the region from about $T_r = 0.7$ to near the critical point, many estimation methods are of a corresponding states type that resemble or are identical with those used in the first sections of this chapter to treat gases. For example, Letsou and Stiel [130] proposed, for *saturated liquids,*

$$\eta_{SL}\xi = (\eta_L\xi)^{(0)} + \omega(\eta_L\xi)^{(1)} \tag{9-12.1}$$

where the parameters $(\eta_L\xi)^{(0)}$ and $(\eta_L\xi)^{(1)}$ are functions only of reduced temperature and ξ is defined in Eq. (9-4.14). Letsou and Stiel tabulate these functions; but to a close approximation, from $0.76 < T_r < 0.98$ they can be expressed as

$$(\eta_L\xi)^{(0)} = 10^{-3}(2.648 - 3.725T_r + 1.309T_r^2) \tag{9-12.2}$$

$$(\eta_L\xi)^{(1)} = 10^{-3}(7.425 - 13.39T_r + 5.933T_r^2) \tag{9-12.3}$$

The units have been converted to yield η_{SL} in centipoises even though ξ [from Eq. (9-4.14)] has the dimensions of micropoises.

This correlation was developed from data on only 14 liquids, mostly simple hydrocarbons. The authors report average errors of about 3 percent for most materials up to $T_r \approx 0.92$; larger errors were found as the critical point was approached. In our testing of this method, using some compounds other than hydrocarbons, larger errors were found, i.e., up to 15 to 20 percent. In general, however, the technique is a simple one to use and yields estimates that are often surprisingly good.

Example 9-19 Estimate the saturated liquid viscosity of n-propanol at 433.2 K by using the Letsou-Stiel correlation. The experimental value is 0.188 cP.

solution From Appendix A, $T_c = 536.8$ K, $P_c = 51.7$ bar, $\omega = 0.623$, and $M = 60.10$. Thus, from Eq. (9-4.14)

$$\xi = (0.176)\left[\frac{(536.8)}{(60.10)^3(51.7)^4}\right]^{1/6} = 4.664 \times 10^{-3}$$

With $T = 433.2$ K and $T_r = 433.2/536.8 = 0.807$ and with Eqs. (9-12.2) and (9-12.3),

$$(\eta_L \xi)^{(0)} = (10)^{-3}[2.648 - (3.725)(0.807) + (1.309)(0.807)^2] = 4.944 \times 10^{-4}$$

$$(\eta_L \xi)^{(1)} = (10)^{-3}[7.425 - (13.39)(0.807) + (5.933)(0.807)^2] = 4.831 \times 10^{-4}$$

$$\eta_{SL} \xi = [4.944 + (0.623)(4.831)](10^{-4}) = 7.954 \times 10^{-4}$$

$$\eta_{SL} = \frac{7.954 \times 10^{-4}}{4.664 \times 10^{-3}} = 0.171 \text{ cP}$$

$$\text{Error} = \frac{0.171 - 0.188}{0.188} \times 100 = -9.0\%$$

A more general estimation method would logically involve the extension of the high-pressure gas viscosity correlations described in Sec. 9-6 into the liquid region. Two techniques have, in fact, been rather widely tested and found reasonably accurate for reduced temperatures above about 0.5. These methods are those of Chung et al. [44] and Brulé and Starling [30]. Both methods use Eq. (9-6.16), but they have slightly different coefficients to compute some of the parameters. The Chung et al. form is preferable for simple molecules and will treat polar as well as nonpolar compounds. The Brulé and Starling relation was developed primarily for complex hydrocarbons, and the authors report their predictions are within 10 percent of experimental values in the majority of cases. The Chung et al. method has a similar accuracy for most nonpolar compounds, but significantly higher errors can occur with polar, halogenated, or high-molecular-weight compounds. In both cases, one needs accurate liquid density data, and the reliability of the methods decreases significantly for T_r less than about 0.5. The liquids need not be saturated; subcooled compressed liquid states simply reflect a higher liquid density.

The Chung et al. technique was illustrated for dense gas ammonia in Example 9-12. The procedure is identical when applied to high-temperature liquids. We present, instead, an example of the use of the Brulé and Starling approach.

Example 9-20 Estimate the viscosity of liquid acenaphthene (a double-ring aromatic compound found in shale oil and tar sand fluids) at 100°C (373.2 K) by using the Brulé-Starling method. At this temperature, the experimental viscosity is 1.39 cP and the liquid density is about 1.03 g/cm³.

solution For acenaphthene, $T_c = 824$ K, $V_c = 460$ cm³/mol, $\omega = 0.36$, and $M = 154.21$. At 373 K, $T_r = (373/824) = 0.453$ and the molar density $\rho_L = 1.03/154.21 = 6.68 \times 10^{-3}$ mol/cm³. We use Eq. (9-6.16) with Table 9-7. F_c is given by Eq. (9-4.10) as

$$F_c = 1 - (0.2756)(0.36) = 0.901$$

$T^* = (1.2593)(0.453) = 0.570$ [Eq. (9-4.8)] and, with Eq. (9-4.3), $\Omega_v = 2.139$. The density is introduced in Eqs. (9-6.18) and (9-6.19),

$$y = \frac{(6.68 \times 10^{-3})(460)}{6} = 0.512$$

$$G_1 = \frac{1 - (0.5)(0.512)}{(1 - 0.512)^3} = 6.40$$

Using Table 9-7, and substituting ω for γ, $E_1 = 29.71$, $E_2 = 1.644 \times 10^{-3}$, $E_3 = 112.0$, $E_4 = 25.02$, $E_5 = 20.62$, $E_6 = -9.71$, $E_7 = 24.15$, $E_8 = 2.134$, $E_9 = -1.368$, and $E_{10} = 0.735$. From Eq. (9-6.20), $G_2 = 1.381$; from Eq. (9-6.21), $\eta^{**} = 64.34$; and from Eq. (9-6.17), $\eta^* = 62.99$. Finally, with Eq. (9-6.16),

$$\eta_L = (62.99) \frac{(36.344)[(154.21)(824)]^{1/2}}{(460)^{2/3}}$$

$$= 13{,}700 \ \mu P = 1.37 \ cP$$

$$\text{Error} = \frac{1.37 - 1.39}{1.39} \times 100 = -1.5\%$$

It might be noted that an error of -15 percent would have been found if the Chung et al. method had been used.

Discussion

The quantity of accurate liquid viscosity data at temperatures much above the normal boiling point is not large. In addition, to test estimation methods such as those of Chung et al. or Brulé and Starling, one needs accurate liquid density data under the same conditions as apply to the viscosity data. This matching makes it somewhat difficult to test the methods with many compounds. However, Brulé and Starling developed their technique so that they would be coupled to a separate computation program using a modified BWR equation of state to provide densities. They report relatively low errors (as noted above), and this fact appears to confirm the general approach (see also Ref. 30). Hwang et al. [102] have proposed viscosity (as well as density and surface tension) correlations for coal liquids.

Regardless of what high-temperature estimation method is chosen, there is the problem of joining both high- and low-temperature estimated viscosities should that be necessary.

9-13 Liquid Mixture Viscosity

Essentially all correlations for liquid mixture viscosity refer to solutions of liquids below or only slightly above their normal boiling points; i.e., they are restricted to reduced temperatures (of the pure components) to values below about 0.7. The bulk of the discussion below is limited to that

temperature range. At the end of the section, however, we suggest approximate methods to treat high-pressure, high-temperature liquid mixture viscosity.

At temperatures below $T_r \approx 0.7$, liquid viscosities are very sensitive to the structure of the constituent molecules (see Sec. 9-11). This generality is also true for liquid mixtures, and even mild association effects between components can often significantly affect the viscosity.

Almost all methods to estimate or correlate liquid mixture viscosities assume that values of the viscosities of the pure components are available. Thus the methods are, in reality, interpolative. Nevertheless, there is no agreement on the best way to carry out the interpolation. Irving [104] surveyed more than 50 equations for binary liquid viscosities and classified them by type. He points out that only very few do not have some adjustable constant that must be determined from experimental data—and the few that do not require such a parameter are applicable only to systems of similar components with comparable viscosities. In a companion report from the National Engineering Laboratory, Irving [105] has also evaluated 25 of the more promising equations with experimental data from the literature. He recommends the one-constant Grunberg-Nissan equation [87] [see Eq. (9-13.1)] as being widely applicable yet reasonably accurate except for aqueous solutions. This NEL report is also an excellent source of viscosity data tabulated from the literature.

Method of Grunberg and Nissan [87]

In this procedure, the low-temperature liquid viscosity for mixtures is given as

$$\ln \eta_m = \sum_i x_i \ln \eta_i + \frac{1}{2} \sum_i \sum_{i \neq j} x_i x_j G_{ij} \tag{9-13.1}$$

or, for a binary of 1 and 2,

$$\ln \eta_m = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 G_{12} \tag{9-13.2}$$

since $G_{ii} = 0$. In Eqs. (9-13.1) and (9-13.2), x is the liquid mole fraction and G_{ij} is an interaction parameter which is a function of the components i and j as well as the temperature (and, in some cases, the composition). This relation has probably been more extensively examined than any other liquid mixture viscosity correlation. Isdale [107] presents the results of a very detailed testing using more than 2000 experimental mixture datum points. When the interaction parameter was regressed from experimental data, nonassociated mixtures and many mixtures containing alcohols, carboxylic acids, and ketones were fitted satisfactorily. The overall root mean square deviation for the mixtures tested was 1.6 percent. More

recently, Isdale et al. [109] proposed a group contribution method to estimate the binary interaction parameter G_{ij} at 298 K.

The procedure to be followed is:

1. For a binary of i and j, select i by following the priority rules below. (j then becomes the second component.)
   - a. i = an alcohol, if present
   - b. i = an acid, if present
   - c. i = the component with the most carbon atoms
   - d. i = the component with the most hydrogen atoms
   - e. i = the component with the most $-CH_3$ groups

   G_{ij} = 0 if none of these rules establish a priority.

2. Once the decision has been made which component is i and which is j, calculate $\Sigma \Delta$ for i and j from the group contributions in Table 9-12.

3. Determine the parameter W. (If either i or j contains atoms other than carbon and hydrogen, set $W = 0$ and go to step 4.) Let the number of carbon atoms in i be N_i and that in j be N_j.

$$W = \frac{(0.3161)(N_i - N_j)^2}{N_i + N_j} - (0.1188)(N_i - N_j) \qquad (9\text{-}13.3)$$

4. Calculate G_{ij} from

$$G_{ij} = \Sigma \Delta_i - \Sigma \Delta_j + W \qquad (9\text{-}13.4)$$

TABLE 9-12   Group Contributions for G_{ij} at 298K

Group	Notes	Value
$-CH_3$		-0.100
$>CH_2$		0.096
$>CH-$		0.204
$>C<$		0.433
Benzene ring		0.766
Substitutions:		
Ortho		0.174
Meta		—
Para		0.154
Cyclohexane ring		0.416
$-OH$	Methanol	0.887
	Ethanol	-0.023
	Higher aliphatic alcohols	-0.443
$>C=O$	Ketones	1.046
$-Cl$		$0.653 - 0.161N_{Cl}$
$-Br$		-0.116
$-COOH$	Acid with:	
	Nonassociated liquids	$-0.411 + 0.06074N_C$
	Ketones	1.130
	Formic acid with ketones	0.167

N_{Cl} = number of chlorine atoms in the molecule
N_C = *total* number of carbon atoms in the binary set

Example 9-21 Estimate the viscosity of a liquid mixture of n-hexane and n-hexadecane as a function of composition. The temperature is 298 K. The viscosities of pure n-hexane and n-hexadecane at this temperature are 0.298 and 3.078 cP [68].

solution We establish that n-hexadecane is to be called component i by using the priority rules above (rule c in this instance). With Table 9-12, we can compute $\Sigma \Delta_i$ and $\Sigma \Delta_j$.

$$\Sigma \Delta_i \ (n\text{-hexadecane}) = (2)(-0.100) + (14)(0.096) = 1.144$$

$$\Sigma \Delta_j \ (n\text{-hexane}) = (2)(-0.100) + (4)(0.096) = 0.184$$

N_i, the number of carbon atoms in n-hexadecane, equals 16, and N_j is 6. With Eq. (9-13.3),

$$W = \frac{(0.3161)(16 - 6)^2}{(16 + 6)} - (0.1188)(16 - 6) = 0.249$$

Then, with Eq. (9-13.4),

$$G_{ij} = 1.144 - 0.184 + 0.249 = 1.209$$

and Eq. (9-13.2) becomes

$$\ln \eta_m = x_1 \ln (0.298) + x_2 \ln (3.078) + (x_1 x_2)(1.209)$$

where subscript 1 refers to n-hexane. The estimated values of η_m are compared with experimental data in the table below. The experimental mixture viscosities were reported by Dymond et al. [68].

Mole fraction n-hexane	Mixture viscosities for n-hexane and n-hexadecane, cP	
	Estimated	Experimental
0.	—	3.078
0.2	2.34	2.24
0.4	1.62	1.51
0.6	1.01	0.991
0.8	0.577	0.584
1.0	—	0.298

In Fig. 9-15, estimated and experimental mixture viscosities are plotted against composition. An excellent fit is seen.

G_{ij} is sometimes a function of temperature. However, existing data suggest that, for alkane-alkane solutions or for mixtures of an associated component with an unassociated one, G_{ij} is independent of temperature. However, for mixtures of nonassociated compounds (but *not* of only alkanes) or for mixtures of associating compounds, G_{ij} is a mild function of temperature. Isdale et al. [109] suggest for these latter two cases,

$$G_{ij} (T) = 1 - [1 - G_{ij}(298)] \frac{573 - T}{275} \tag{9-13.5}$$

where T is in kelvins.

Example 9-22 Estimate the viscosity of a mixture of acetic acid and acetone at 323 K (50°C) that contains 70 mole percent acetic acid. Isdale et al. quote the experimental value to be 0.587 cP, and, at 50°C, the viscosities of pure acetic acid and acetone are 0.798 and 0.241 cP, respectively.

solution First we must estimate G_{ij} at 298 K. Component i is acetic acid (priority rule b). Since the mixture contains atoms other than carbon and hydrogen (i.e., oxygen), $W = 0$. Then, with Table 9-12,

$$\Sigma \, \Delta_i \text{ (acetic acid)} = -CH_3 + -COOH = -0.100 + 1.130 = 1.030$$

$$\Sigma \, \Delta_j \text{ (acetone)} = (2)(-CH_3) + {>}C{=}0 = (2)(-0.100) + 1.046 = 0.846$$

With Eq. (9-13.4),

$$G_{ij} = 1.030 - 0.846 = 0.184 \text{ at 298 K}$$

At 50°C = 323 K, we need to adjust G_{ij} with Eq. (9-13.5).

$$G_{ij}(323 \text{ K}) = 1 - \frac{(1 - 0.184)(573 - 323)}{275} = 0.258$$

Then, using Eq. (9-13.2),

$$\ln \eta_m = (0.7) \ln (0.798) + (0.3) \ln (0.241) + (0.7)(0.3)(0.258) = -0.531$$

$$\eta_m = 0.588 \text{ cP}$$

This estimated value is essentially identical with the experimental result of 0.587 cP.
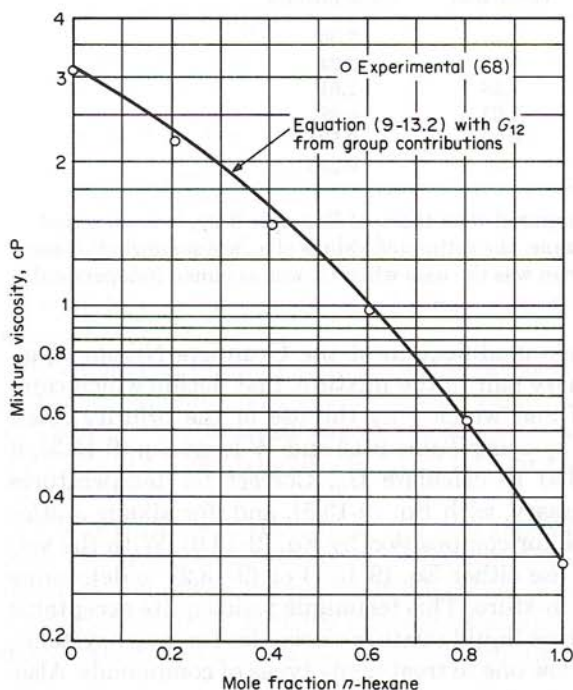

Figure 9-15 Liquid mixture viscosity of n-hexane and n-hexadecane at 298 K.

Generally, one assumes the estimated value of G_{ij} is independent of composition. However, for special cases of mixtures of normal and/or branched chain alkanes, the estimated value of G_{ij} should be corrected for composition by Eq. (9-13.6) [109].

$$G_{ij}(x_i) = G_{ij}(1.343 - 0.685x_i) \qquad (9\text{-}13.6)$$

where G_{ij} is the value of the interaction parameter from Eq. (9-13.4) and x_i is the mole fraction of the component identified as i. No temperature correction is necessary because, for alkane mixtures, G_{ij} is independent of temperature. $G_{ij}(x_i)$ is the interaction parameter at a composition x_i. Note that $G_{ij}(x_i) = G_{ij}$ when $x_i = 0.5$, so the effect of using Eq. (9-13.6) is more pronounced at either larger or smaller values of x_i.

Example 9-23   Repeat Example 9-21 but allow for variations in G_{ij} with composition.

solution   In Example 9-21 for the system $i = n$-hexadecane and $j = n$-hexane, G_{ij} was computed to be 1.209. With Eqs. (9-13.6) and (9-13.2), the calculated $G_{ij}(x_i)$ and η_m values are as shown below.

Mole fraction n-hexane	$G_{ij}(x_i)$	η_m, cP	
		Estimated	Experimental
0.	—	—	3.08
0.2	0.961	2.19	2.24
0.4	1.127	1.59	1.51
0.6	1.292	1.03	0.991
0.8	1.458	0.60	0.584
1.0	—	—	0.298

When these results are compared with those of Example 9-21, it is seen that, at low mole fractions of n-hexane, the estimated values of η_m are somewhat closer to the experimental results than was the case when G_{ij} was assumed independent of composition.

To summarize the Isdale modification of the Grunberg-Nissan equation, for each possible binary pair in the mixture, first decide which component is to be labeled i and which j by the use of the priority rules. Determine $\Sigma \Delta_i$ and $\Sigma \Delta_j$ by using Table 9-12 and W from Eq. (9-13.3), if necessary. Use Eq. (9-13.4) to calculate G_{ij}. Correct for temperatures other than 298 K, if necessary, with Eq. (9-13.5), and, for alkane and/or branched alkane mixtures, for composition by Eq. (9-13.6). With the values of G_{ij} so determined, use either Eq. (9-13.1) or (9-13.2) to determine the viscosity of the liquid mixture. This technique yields quite acceptable estimates of low-temperature liquid mixture viscosities for many systems, but Table 9-12 does not allow one to treat many types of compounds. Also, the method does not cover aqueous mixtures.

Method of Teja and Rice [197, 198]

Based on a corresponding states treatment for mixture compressibility factors [196, 199], Teja and Rice propose an analogous form for liquid mixture viscosity.

$$\ln (\eta_m \epsilon_m) = \ln (\eta \epsilon)^{(r_1)} + [\ln (\eta \epsilon)^{(r_2)} - \ln (\eta \epsilon)^{(r_1)}] \frac{\omega_m - \omega^{(r_1)}}{\omega^{(r_2)} - \omega^{(r_1)}} \qquad (9\text{-}13.7)$$

where the superscripts (r_1) and (r_2) refer to two reference fluids. η is the viscosity, ω the acentric factor, and ϵ is a parameter similar to ξ in Eq. (9-4.14) but defined here as:

$$\epsilon = \frac{V_c^{2/3}}{(T_c M)^{1/2}} \qquad (9\text{-}13.8)$$

The variable of composition is introduced in four places: the definitions of ω_m, V_{cm}, T_{cm}, and M_m. The rules suggested by the authors to compute these mixture parameters are:

$$V_{cm} = \sum_i \sum_j x_i x_j V_{cij} \qquad (9\text{-}13.9)$$

$$T_{cm} = \frac{\sum_i \sum_j x_i x_j T_{cij} V_{cij}}{V_{cm}} \qquad (9\text{-}13.10)$$

$$M_m = \sum_i x_i M_i \qquad (9\text{-}13.11)$$

$$\omega_m = \sum_i x_i \omega_i \qquad (9\text{-}13.12)$$

$$V_{cij} = \frac{(V_{ci}^{1/3} + V_{cj}^{1/3})^3}{8} \qquad (9\text{-}13.13)$$

$$T_{cij} V_{cij} = \psi_{ij} (T_{ci} T_{cj} V_{ci} V_{cj})^{1/2} \qquad (9\text{-}13.14)$$

ψ_{ij} is an interaction parameter of order unity which must be found from experimental data.

It is important to note that, in the use of Eq. (9-13.7) for a given mixture at a specified temperature, the viscosity values for the two reference fluids $\eta^{(r_1)}$ and $\eta^{(r_2)}$ are to be obtained *not at* T, but at a temperature equal to $T[(T_c)^{(r_1)}/T_{cm}]$ for (r_1) and $T[(T_c)^{(r_2)}/T_{cm}]$ for (r_2). T_{cm} is given by Eq. (9-13.10).

Whereas the reference fluids (r_1) and (r_2) may be chosen as different from the actual components in the mixture, it is normally advantageous to select them from the principal components in the mixture. In fact, for a binary of 1 and 2, if (r_1) is selected as component 1 and (r_2) as component 2, then, by virtue of Eq. (9-13.12), Eq. (9-13.7) simplifies to

$$\ln (\eta_m \epsilon_m) = x_1 \ln (\eta \epsilon)_1 + x_2 \ln (\eta \epsilon)_2 \qquad (9\text{-}13.15)$$

but, as noted above, η_1 is to be evaluated at $T(T_{c_1}/T_{cm})$ and η_2 at $T(T_{c2}/T_{cm})$.

Our further discussion of this method will be essentially limited to Eq. (9-13.15), since that is the form most often used for binary liquid mixtures and, by this choice, one is assured that the relation gives correct results when $x_1 = 0$ or 1.0. In addition, the assumption is made that the interaction parameter ψ_{ij} is not a function of temperature or composition.

The authors claim good results for many mixtures ranging from strictly nonpolar to highly polar aqueous-organic systems. For nonpolar mixtures, errors averaged about 1 percent. For nonpolar-polar and polar-polar mixtures, the average rose to about 2.5 percent, whereas for systems containing water, an average error of about 9 percent was reported.

In comparison with the Grunberg-Nissan correlation [Eq. (9-13.1)], with G_{ij} found by regressing data, Teja and Rice show that about the same accuracy is achieved for both methods for nonpolar-nonpolar and nonpolar-polar systems, but their technique was significantly more accurate for polar-polar mixtures, and particularly for aqueous solutions for which Grunberg and Nissan's form should not be used.

Example 9-24 Estimate the viscosity of a liquid mixture of water and 1,4-dioxane at 60°C when the mole fraction water is 0.83. For this very nonideal solution, Teja and Rice suggest an interaction parameter $\psi_{ij} = 1.37$.

solution From Appendix A, for water, $T_c = 647.1$ K, $V_c = 56$ cm³/mol, and $M = 18.02$; for 1,4-dioxane, $T_c = 587$ K, $V_c = 238$ cm³/mol, and $M = 88.11$. Let 1 be water and 2 be 1,4-dioxane. With Eq. (9-13.8), $\epsilon_1 = (56)^{2/3}/[(647.1)(18.02)]^{1/2} = 0.136$; $\epsilon_2 = 0.169$. From Eq. (9-13.9),

$$V_{cm} = (0.830)^2(56) + (0.170)^2(238) + (2)(0.830)(0.170) \times \frac{[(56)^{1/3} + (238)^{1/3}]^3}{8}$$

$$= 80.98 \text{ cm}^3/\text{mol}$$

and, with Eq. (9-13.10),

$$T_{cm} = \{(0.830)^2(647.1)(56) + (0.170)^2(587)(238)$$

$$+ (2)(0.830)(0.170)(1.37)[(647.1)(56)(587)(238)]^{1/2}\}/80.98$$

$$= 697.8 \text{ K}$$

$$M_m = (0.830)(18.02) + (0.170)(88.11) = 29.94$$

so, with Eq. (9-13.8),

$$\epsilon_m = \frac{(80.98)^{2/3}}{[(697.8)(29.94)]^{1/2}} = 0.130$$

Next, we need to know the viscosity of water not at 333.2 K (60°C), but at a temperature of $(333.2)(647.1)/697.8 = 309.0$ K (35.8°C). This value is 0.712 cP [105]. [Note that, at 60°C, η (water) = 0.468 cP.] For 1,4-dioxane, the reference temperature is $(333.2)(587)/697.8 = 280.3$ K (7.1°C), and at that temperature, $\eta = 1.63$ cP [105]. Again this value is quite different from the viscosity of 1,4-dioxane at 60°C, which is 0.715 cP.

Finally, with Eq. (9-13.15),

$$\ln\left[(\eta_m)(0.130)\right] = (0.830)\ln\left[(0.712)(0.136)\right] + (0.170)\ln\left[(1.63)(0.169)\right]$$

$$= -2.157$$

$$\eta_m = 0.90 \text{ cP}$$

The experimental viscosity is 0.89 cP.

Although the agreement between the experimental and estimated viscosity in Example 9-24 is excellent, in other composition ranges, higher errors occur. In Fig. 9-16 we have plotted the estimated and experimental values of the mixture viscosity over the entire range of composition. From a mole fraction water of about 0.8 (weight fraction = 0.45) to unity, the method provides an excellent fit to experimental results. At smaller concentrations of water, the technique overpredicts η_m. Still, for such a nonideal aqueous mixture, the general fit should be considered good.
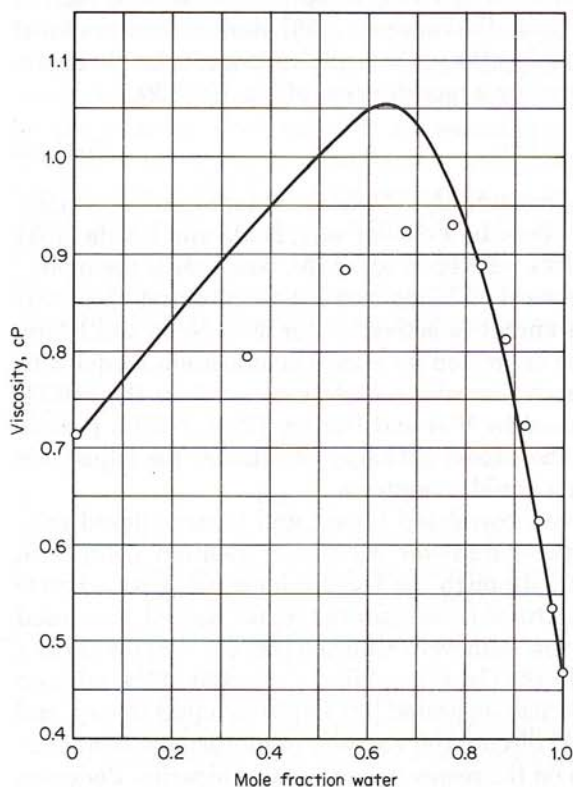

Figure 9-16   Viscosity of water and 1,4-dioxane at 333 K.
———— Eq. (9-13.15); $\psi_{ij} = 1.37$; o experimental [105]

Discussion

Two methods have been introduced to estimate the viscosity of liquid mixtures: the Grunberg-Nissan relation [Eq. (9-13.1)] and the Teja-Rice form [Eq. (9-13.15)]. Both contain one adjustable parameter per binary pair in the mixture. An approximate technique is available to estimate the Grunberg-Nissan parameter G_{ij} as a function of temperature [Eq. (9-13.5)] for many types of systems. Teja and Rice suggest that their parameter ψ_{ij} is independent of temperature—at least over reasonable temperature ranges. This latter technique seems to be better for highly polar systems, especially if water is one of the components, and it has also been applied to undefined mixtures [200, 205] with the introduction of reference components [see Eq. (9-13.7)].

Stairs [183] proposed another one-parameter mixture correlation, but it may be shown that his relations reduce to the Grunberg-Nissan form when mole fractions are used as composition variables. Vogel and Weiss [218] correlated their mixture viscosity data with the Grunberg-Nissan equation and, for systems of quite spherical molecules, show G_{ij} is related to the excess entropy of mixing. Pikkarainen [159] studied very nonideal systems of N-methylacetamide with various aliphatic alcohols. He determined a parameter Q defined by a modification of Eq. (9-13.2),

$$Q = \ln \nu_m - x_1 \ln \nu_1 - x_2 \ln \nu_2 \tag{9-13.16}$$

where ν is the kinematic viscosity, η/ρ. Q was then expressed as a polynomial in x_1 for several systems. In a similar way, Noda and Ishida [151] use Eq. (9-13.16) except that ν was replaced by νM, where M is the molecular weight. Both Pikkarainen and Noda and Ishida interpret Q as $\Delta G/RT$, where ΔG is the Gibbs energy of activation for flow. Noda and Ishida then propose that Q/RT be expressed by a local composition model with two adjustable parameters. A viscosity correlation based on the NRTL correlation has been proposed by Wei and Rowley [220]. NRTL parameters are necessary, as is the excess enthalpy of mixing. An adjustable parameter is used for highly nonideal systems.

Several recent studies have correlated binary and ternary liquid mixture viscosities with the two-parameter McAllister relation [140] with good results [6, 57, 58, 152], although the Dizechi form [56] gave a better fit for very polar mixtures. Other investigators [16, 65, 68, 94] have used Eq. (9-11.9) for mixtures. New data were reported [66, 67, 108] for various systems and correlated with the Grunberg-Nissan equation. New mixture correlation techniques were also suggested [86, 96] from liquid theory, and Kestin and Shankland [123] discuss the viscosity of multicomponent electrolyte solutions from data on the respective salt-water binaries. Pedersen et al. [158] present a correlation technique to estimate the viscosity of crude oils.

To finish this section, we again reiterate that the methods proposed should be limited to situations in which the reduced temperatures of the components comprising the mixture are less than about 0.7, although the exact temperature range of the Teja-Rice procedure is as yet undefined.

Should one desire the viscosity of liquid mixtures at high pressures and temperatures, it is possible to employ the Chung et al. method [44] described in Sec. 9-7 to estimate high-pressure gas mixture viscosities. This recommendation is tempered by the fact that such a procedure has been only slightly tested, and usually with rather simple systems where experimental data exist.

Recommendations to estimate the viscosities of liquid mixtures

To estimate low-temperature liquid mixture viscosities, either the Grunberg-Nissan equation [Eq. (9-13.1) or (9-13.2)] or the Teja-Rice relation [Eq. (9-13.7) or (9-13.15)] may be used. Both require some experimental data to establish the value of an interaction parameter specific for each binary pair in the mixture. In many instances, however, it is possible to estimate the Grunberg-Nissan interaction parameter G_{ij} by a group contribution technique and thus alleviate any necessity to have viscosity data for the mixture. Both methods are essentially interpolative in nature, so viscosities of the pure components comprising the mixture must be known. (Or in the Teja-Rice procedure, one may instead use reference fluids of similar structure rather than the actual mixture components.) The errors to be expected range from a few percent for nonpolar or slightly polar mixtures to 5 to 10 percent for polar mixtures. With aqueous solutions, the Grunberg-Nissan form is not recommended.

Notation

a^*	group contribution sum; Eq. (9-4.21)
b_0	excluded volume, $(2/3)\pi N_0\sigma^3$
B	viscosity parameter in Eq. (9-11.2)
C_v	heat capacity at constant volume, $J/(mol\cdot K)$; C_i, structural contribution in Eq. (9-4.21) and Table 9-3
D	diffusion coefficient, cm^2/s or m^2/s
F_c	shape and polarity factor in Eq. (9-4.10); F_P°, low-pressure polar correction factor in Eq. (9-4.17); F_Q°, low-pressure quantum correction factor in Eq. (9-4.18); F_P, high-pressure polar correction factor in Eq. (9-6.8); F_Q, high-pressure quantum correction factor in Eq. (9-6.9)
G_1, G_2	parameters in Eqs. (9-6.19) and (9-6.20)
ΔG	Gibbs energy of activation for flow, J/mol

k	Boltzmann's constant
L	mean free path
m	mass of molecule
M	molecular weight
n	number density of molecules; number of components in a mixture
N	number of carbon atoms; N^*, equivalent chain length; ΔN_i, structural contribution in Eq. (9-11.3) and Table 9-10; N_0; Avogadro's number
P	pressure, N/m^2 or bar (unless otherwise specified); P_c, critical pressure; P_r, reduced pressure, P/P_c; P_{vp}, vapor pressure; $\Delta P_r = (P - P_{vp})/P_c$
Q	polar parameter in Eq. (9-6.3); parameter in Eq. (9-13.16)
r	distance of separation
R	gas constant, usually 8.314 J/(mol·K)
T^*	kT/ϵ
T	temperature, K; T_c, critical temperature; T_r, reduced temperature, T/T_c; T_0, parameter in Eq. (9-11.2)
v	molecular velocity
V	volume, cm^3/mol; V_c, critical volume; V_r, reduced volume, V/V_c
x	mole fraction, liquid
y	mole fraction, vapor; parameter in Eq. (9-6.18)
Y	parameter in Eq. (9-6.7)
Z	compressibility factor; Z_c, critical compressibility factor; Z_1, Z_2, parameters in Eqs. (9-6.4) and (9-6.7)

GREEK

γ	orientation factor in the Brulé-Starling method, Table 9-7, or obtain from Ref. 30
Δ	correction term in Eq. (9-6.15)
ϵ	energy-potential parameter; variable defined in Eq. (9-13.8)
η	viscosity (usually in micropoises for gas and in centipoises for liquids); $\eta°$, denotes value at low-pressure (about 1 bar); η_c, at the critical point; $\eta_c°$, at the critical temperature but at about 1 bar; η^*, η^{**}, parameters in Eqs. (9-6.17) and (9-6.21)
κ	polar correction factor in Eq. (9-4.10), see Table 9-1
λ	thermal conductivity, W/(m·K)
μ	dipole moment, debyes; μ_r, dimensionless dipole moment defined in either Eq. (9-4.11) or Eq. (9-4.16)
ν	kinematic viscosity, η/ρ, m^2/s
ξ	inverse viscosity, defined in Eq. (9-4.13) or Eq. (9-4.14); ξ_T, inverse viscosity defined in Eq. (9-6.11)

ρ	density (usually mol/cm^3); ρ_c, critical density; ρ_r, reduced density, ρ/ρ_c
σ	molecular diameter, Å
Ψ	radial distribution function
ψ	intermolecular potential energy as a function of r
ψ_{ij}	interaction parameter in Eq. (9-13.14)
ω	acentric factor, Sec. 2-3
Ω_v	collision integral for viscosity

SUBSCRIPTS

i, j, k	components i, j, k
1, 2	components 1, 2
L	liquid
m	mixture
SL	saturated liquid

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Thermal Conductivity

10-1 Scope

Thermal conductivities of both gases and liquids are considered in this chapter. Some background relevant to the theory of thermal conductivity is given in Secs. 10-2 and 10-3 (for gases) and in Sec. 10-8 (for liquids). Estimation techniques for pure gases at near ambient pressures are covered in Sec. 10-4; the effects of temperature and pressure are discussed in Secs. 10-4 and 10-5. Similar topics for liquids are in Secs. 10-9 to 10-11. Thermal conductivities for gas and for liquid mixtures are covered in Secs. 10-6, 10-7, and 10-12. Thermal conductivities of reacting gas mixtures are not covered. For a recent review, see Ref. 35.

The units used for thermal conductivity are $W/(m \cdot K)$. To convert these to English or cgs units:

$$W/(m \cdot K) \times 0.5778 = Btu/(hr \cdot ft \cdot °R)$$
$$W/(m \cdot K) \times 0.8604 = kcal/(cm \cdot hr \cdot K)$$
$$W/(m \cdot K) \times 2.390 \times 10^{-3} = cal/(cm \cdot s \cdot K)$$

or

$$Btu/(hr \cdot ft \cdot °R) \times 1.731 = W/(m \cdot K)$$
$$kcal/(cm \cdot hr \cdot K) \times 1.162 = W/(m \cdot K)$$
$$cal/(cm \cdot s \cdot K) \times 418.4 = W/(m \cdot K)$$

10-2   Theory of Thermal Conductivity

In Sec. 9-3, through rather elementary arguments, the thermal conductivity of an ideal gas was found to be equal to $vLC_v n/3$ [Eq. (9-3.7)], where v is the average molecular velocity, L is the mean free path, C_v is the heat capacity per molecule, and n is the number density of molecules. Similar relations were derived for the viscosity and diffusion coefficients of gases. In the case of the last two properties, this elementary approach yields approximate but reasonable values. For thermal conductivity, it is quite inaccurate. A more detailed treatment is necessary to account for the effect of having a wide spectrum of molecular velocities; also, molecules may store energy in forms other than translational. For *monatomic gases*, which have no rotational or vibrational degrees of freedom, a more rigorous analysis yields

$$\lambda = \frac{25}{32} (\pi m k T)^{1/2} \frac{C_v/m}{\pi \sigma^2 \Omega_v} \tag{10-2.1}$$

or, written for computational ease, with $C_v = \frac{3}{2} k$,

$$\lambda = 2.63 \times 10^{-23} \frac{(T/M')^{1/2}}{\sigma^2 \Omega_v} \tag{10-2.2}$$

where λ = thermal conductivity, W/(m·K)
$\quad$ T = temperature, K
$\quad$ k = Boltzmann's constant = 1.3805×10^{-23} J/K
$\quad$ M' = molecular weight, kg/mol
$\quad$ σ = characteristic dimension of molecule, m
$\quad$ Ω_v = collision integral, dimensionless

For a hard-sphere molecule, Ω_v is unity; normally, however, it is a function of temperature, and the exact dependence is related to the intermolecular force law chosen. If the Lennard-Jones 12-6 potential [Eq. (9-4.2)] is selected, Ω_v is given by Eq. (9-4.3).

If Eq. (10-2.1) is divided by Eq. (9-3.9),

$$\frac{\lambda M'}{\eta C_v} = 2.5 \tag{10-2.3}$$

With $\gamma = C_p/C_v$, the Prandtl number N_{Pr} is

$$N_{Pr} = \frac{C_p \eta}{\lambda M'} = \frac{\gamma}{2.5} \tag{10-2.4}$$

Since γ for monatomic gases is close to $\frac{5}{3}$ except at very low temperatures, Eq. (10-2.4) would indicate that $N_{Pr} \approx \frac{2}{3}$, a value close to that found experimentally. To obtain Eq. (10-2.3), the terms σ^2 and Ω_v have been elimi-

nated, and the result is essentially independent of the intermolecular potential law chosen.

The dimensionless† group $\lambda M'/\eta C_v$ is known as the *Eucken factor;* it is close to 2.5 for monatomic gases, but it is significantly less for polyatomic gases. Our discussion so far has considered only energy associated with translational motion; since heat capacities of polyatomic molecules exceed those for monatomic gases, a substantial fraction of molecular energy resides in modes other than translational.

10-3 Thermal Conductivities of Polyatomic Gases

Eucken and modified Eucken models

Eucken proposed that Eq. (10-2.3) be modified for polyatomic gases by separating the translational and internal energy contributions into separate terms:

$$\frac{\lambda M'}{\eta C_v} = f_{\text{tr}}\left(\frac{C_{\text{tr}}}{C_v}\right) + f_{\text{int}}\left(\frac{C_{\text{int}}}{C_v}\right) \tag{10-3.1}$$

Thus the translational energy contribution has been decoupled from any internal energy interaction [31, 74, 94, 116, 150, 156, 175, 176], although the validity of this step has been questioned [53, 84, 148, 159]. Invariably, f_{tr} is set equal to 2.5 to force Eq. (10-3.1) to reduce to Eq. (10-2.3) for a monatomic ideal gas. C_{tr} is set equal to the classical value of $\frac{3}{2}R$, and C_{int} is conveniently expressed as $C_v - C_{\text{tr}}$. Then

$$\begin{aligned}\frac{\lambda M'}{\eta C_v} &= \frac{15/4}{C_v/R} + f_{\text{int}}\left(1 - \frac{3/2}{C_v/R}\right) \\ &= \frac{15/4}{(C_p/R) - 1} + f_{\text{int}}\left[1 - \frac{3/2}{(C_p/R) - 1}\right]\end{aligned} \tag{10-3.2}$$

where the ideal-gas relation $(C_p - C_v = R)$ has been used.

Eucken chose $f_{\text{int}} = 1.0$, whereby Eq. (10-3.2) reduces to

$$\frac{\lambda M'}{\eta C_v} = 1 + \frac{9/4}{C_v/R} = 1 + \frac{9/4}{(C_p/R) - 1} \tag{10-3.3}$$

the well-known *Eucken correlation* for polyatomic gases.

Many of the assumptions leading to Eq. (10-3.3) are open to question, in particular, the choice of $f_{\text{int}} = 1.0$. Ubbelohde [166], Chapman and

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†The group $\lambda M'/\eta C_v$ is dimensionless; with SI units, λ is in $\text{W}/(\text{m}\cdot\text{K}) = \text{N}/(\text{s}\cdot\text{K})$, η is in $\text{N}\cdot\text{s}/\text{m}^2$, C_v is in $\text{J}/(\text{mol}\cdot\text{K})$, and M' is in kg/mol.

Cowling [23], Hirschfelder [53], and Schafer [153] have suggested that molecules with excited internal energy states could be regarded as separate chemical species, and the transfer of internal energy is then analogous to a diffusional process. This concept leads to a result that

$$f_{int} = \frac{M' \rho D}{\eta} \tag{10-3.4}$$

where M' = molecular weight, kg/mol
$\quad\quad \eta$ = viscosity, $N \cdot s/m^2$†
$\quad\quad \rho$ = molar density, mol/m^3
$\quad\quad D$ = diffusion coefficient, m^2/s

Most early theories selected D to be equivalent to the molecular self-diffusion coefficient, and f_{int} is then the reciprocal of the Schmidt number. With Eqs. (9-3.9) and (11-3.2) it can be shown that $f_{int} \approx 1.32$ and is almost independent of temperature. With this formulation, Eq. (10-3.2) becomes

$$\frac{\lambda M'}{\eta C_v} = 1.32 + \frac{1.77}{C_v/R} = 1.32 + \frac{1.77}{(C_p/R) - 1} \tag{10-3.5}$$

Equation (10-3.5), often referred to as the *modified Eucken* correlation, was used by Svehla [159] in his compilation of high-temperature gas properties.

The modified Eucken relation [Eq. (10-3.5)] predicts larger values of λ than the Eucken form [Eq. (10-3.3)], and the difference becomes greater as C_v increases above the monatomic gas value of about 12.6 J/(mol·K). Both yield Eq. (10-2.3) when $C_v = \frac{3}{2}R$. Usually, experimental values of λ lie between those calculated by the two Eucken forms except for polar gases, when both predict λ values that are too high. For nonpolar gases, Stiel and Thodos [157] suggested a compromise between Eqs. (10-3.3) and (10-3.5) as

$$\frac{\lambda M'}{\eta C_v} = 1.15 + \frac{2.03}{C_v/R} = 1.15 + \frac{2.03}{(C_p/R) - 1} \tag{10-3.6}$$

Equations (10-3.3), (10-3.5), and (10-3.6) indicate that the Eucken factor $(\lambda M'/\eta C_v)$ should decrease with increasing temperature as the heat capacity rises, but experimental data indicate that the Eucken factor is often remarkably constant with temperature, and, if anything, it increases slightly with temperature. In Fig. 10-1 we illustrate the case for ethyl chloride, where the data of Vines and Bennett show the Eucken factor

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†*Note:* 1 $N \cdot s/m^2$ = 10 poises = 10^3 cP.

increases from only about 1.41 to 1.48 from 40 to 140°C. On this same graph, the predictions of Eqs. (10-3.3), (10-3.5), and (10-3.6) are plotted and, as noted earlier, all predict a small decrease in the Eucken factor as temperature increases. In Fig. 10-2 we have graphed the experimental Eucken factor as a function of *reduced* temperature for 13 quite diverse low-pressure gases. Except for ethane, all show a small rise with an increase in temperature.

Mason and Monchick analysis

In a pioneer paper published in 1962 [94], Mason and Monchick employed the formal dynamic treatment of Wang Chang and Uhlenbeck [177] and Taxman [160] to derive an approximation to the thermal conductivity of polyatomic gases. In the formalism of Eq. (10-3.1) they found

$$f_{tr} = \frac{5}{2}\left[1 - \frac{10}{3\pi}\left(1 - \frac{2}{5}\frac{M'\rho D}{\eta}\right)\frac{C_{rot}}{RZ_{rot}}\right] \tag{10-3.7}$$

$$f_{int} = \frac{M'\rho D}{\eta}\left[1 + \frac{5}{\pi}\left(1 - \frac{2}{5}\frac{M'\rho D}{\eta}\right)\frac{C_{rot}}{C_{int}Z_{rot}}\right] \tag{10-3.8}$$
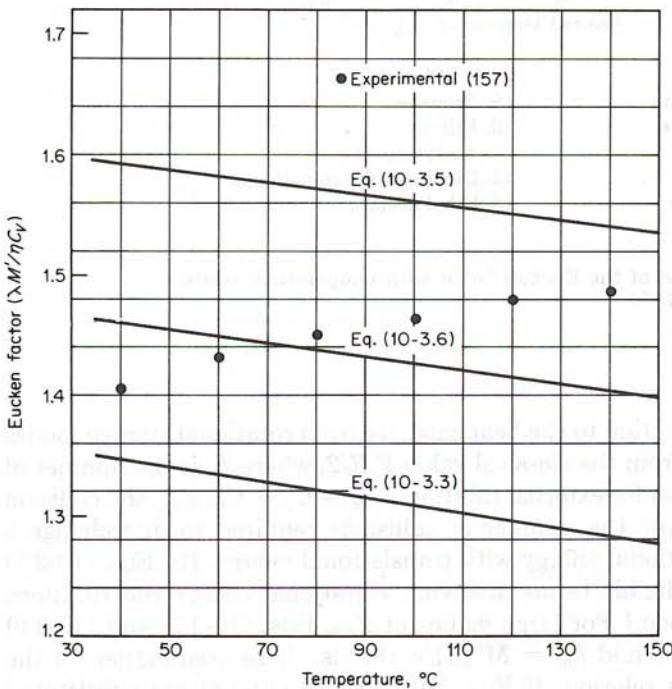
Figure 10-1 Eucken factor for ethyl chloride at low pressure.
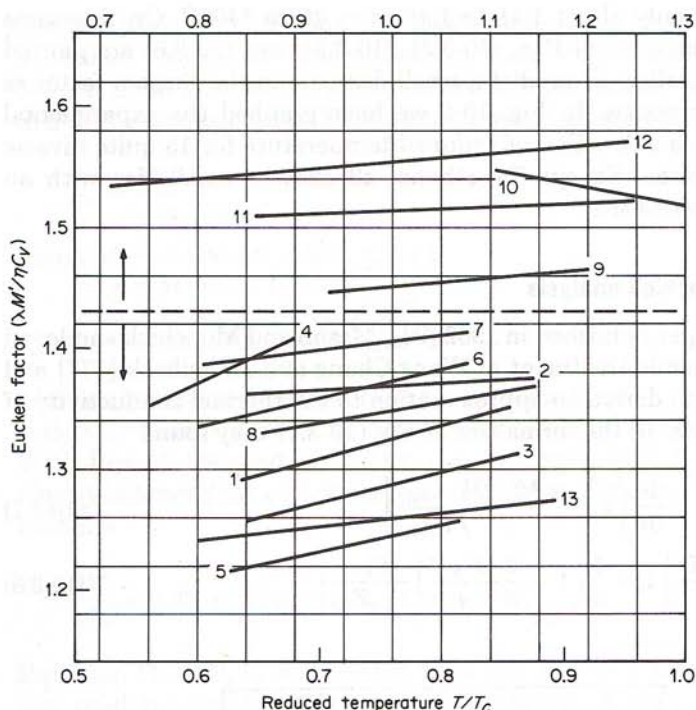
Figure 10-2 Variation of the Eucken factor with temperature. *(Data primarily from Ref. 157.)*

C_{rot} is the contribution to the heat capacity from rotational storage modes and is obtained from the classical value $F_r R/2$, where F_r is the number of degrees of freedom for external rotation. $C_{int} = C_v - C_{tr}$. Z_{rot}, the collision number, represents the number of collisions required to interchange a quantum of rotational energy with translational energy. [In Eqs. (10-3.7) and (10-3.8) negligible terms involving vibrational energy contributions have been dropped.] For large values of Z_{rot}, Eqs. (10-3.7) and (10-3.8) reduce to $f_{tr} = 2.5$ and $f_{int} = M' \rho D/\eta$, that is, those used earlier for the modified Eucken relation. If Eqs. (10-3.7) and (10-3.8) are substituted

into Eq. (10-3.1) and $M' \rho D/\eta$ is assumed to be 1.32,

$$\frac{\lambda M'}{\eta C_v} = 1.32 + \frac{1.77}{C_v/R} - \frac{0.886(C_{rot}/C_v)}{Z_{rot}} \tag{10-3.9}$$

Equation (10-3.9) should be used only for *nonpolar* polyatomic molecules. The key to its use is the accurate estimation of the rotational collision number. To date, this is not possible, although many authors discuss the problem [8, 14, 16, 33, 94, 95, 116, 117, 125, 146, 148, 149, 150, 156]. In Fig. 10-3, we show the Eucken factor $\lambda M'/\eta C_v$ for hydrogen, nitrogen, and carbon dioxide. As noted earlier, most experimental data indicate values of $\lambda M'/\eta C_v$ between those predicted by the Eucken and the modified
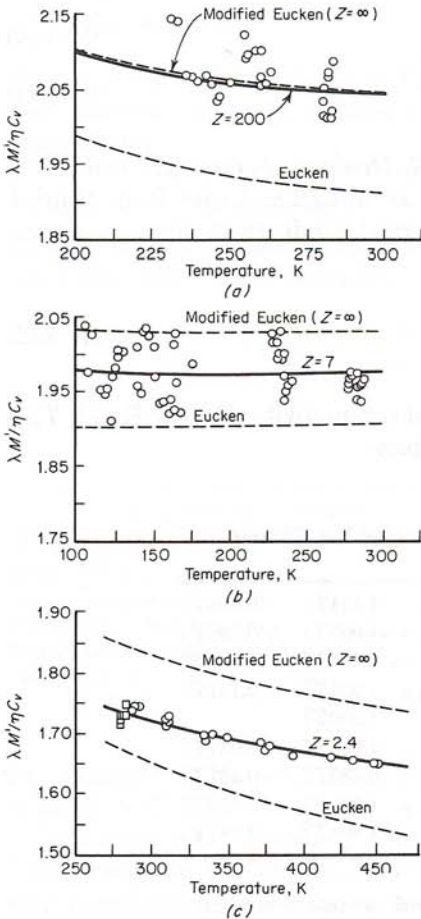
Figure 10-3 Eucken factors as functions of temperature: (a) hydrogen, (b) nitrogen, (c) carbon dioxide. (*From Ref. 14.*)

Eucken relations. In Fig. 10-3, the Z_{rot} shown is that which gave the best fit to the experimental data. Z_{rot} was assumed temperature-independent.

Although Eq. (10-3.8) is probably the best theoretical equation available for estimating the thermal conductivity of a nonpolar polyatomic gas, without some a priori knowledge of Z_{rot}, it is not of much practical value. Z_{rot} values normally lie between 1 and 10 and are probably temperature-dependent [8, 52]; widely differing values are reported in the literature. Attempts to relate Z_{rot} to other, more readily available properties of a molecule have not been successful.

Roy and Thodos estimation technique

In the same way that the viscosity was nondimensionalized in Eqs. (9-4.12) and (9-4.13), a reduced thermal conductivity may be expressed as

$$\lambda_r = \lambda \Gamma \tag{10-3.10}$$

$$\Gamma = \left[\frac{T_c \, (M')^3 \, N_0^2}{R^5 P_c^4} \right]^{1/6} \tag{10-3.11}$$

In SI units, if $R = 8314$ J/(kmol·K), N_0 (Avogadro's number) $= 6.023 \times 10^{26}$ (kmol)$^{-1}$, and with T_c in kelvins, M' in kg/kmol, and P_c in N/m², Γ has the units of m·K/W or inverse thermal conductivity. In more convenient units,

$$\Gamma = 210 \left(\frac{T_c M^3}{P_c^4} \right)^{1/6} \tag{10-3.12}$$

where Γ is the reduced, inverse thermal conductivity, [W/(m·K)]$^{-1}$, T_c is in kelvins, M is in g/mol, and P_c is in bars.

TABLE 10-1   Recommended $f(T_r)$ Equations for the Roy-Thodos Method

Saturated hydrocarbons†	$-0.152T_r + 1.191T_r^2 - 0.039T_r^3$
Olefins	$-0.255T_r + 1.065T_r^2 + 0.190T_r^3$
Acetylenes	$-0.068T_r + 1.251T_r^2 - 0.183T_r^3$
Naphthalenes and aromatics	$-0.354T_r + 1.501T_r^2 - 0.147T_r^3$
Alcohols	$1.000T_r^2$
Aldehydes, ketones, ethers, esters	$-0.082T_r + 1.045T_r^2 + 0.037T_r^3$
Amines and nitriles	$0.633T_r^2 + 0.367T_r^3$
Halides	$-0.107T_r + 1.330T_r^2 - 0.223T_r^3$
Cyclic compounds‡	$-0.354T_r + 1.501T_r^2 - 0.147T_r^3$

†Not recommended for methane.
‡For example, pyridine, thiophene, ethylene oxide, dioxane, piperidine.

The reduced thermal conductivity was employed by Roy and Thodos [142, 143], who, however, separated the $\lambda\Gamma$ product into two parts. The first, attributed only to translational energy, was obtained from a curve fit of the data for the rare gases [141]; this part varies only with the reduced temperature, $T = T/T_c = T_r$. In the second, the contribution from rotational, vibrational, etc., interchange was related to the reduced temperature and a specific constant estimated from group contributions. The final equation may be written

$$\lambda_r = \lambda\Gamma = (\lambda\Gamma)_{tr} + (\lambda\Gamma)_{int} \tag{10-3.13}$$

where λ = low-pressure gas thermal conductivity, $W/(m\cdot K)$ and Γ is defined in Eq. (10-3.12).

$$(\lambda\Gamma)_{tr} = 8.757[\exp{(0.0464T_r)} - \exp{(-0.2412T_r)}] \tag{10-3.14}$$

$$(\lambda\Gamma)_{int} = Cf(T_r) \tag{10-3.15}$$

Relations for $f(T_r)$ are shown in Table 10-1. The constant C is specific for each material, and it is estimated by a group contribution technique as shown below.

Estimation of Roy-Thodos constant C. T In the discussion to follow, one identifies carbon types as shown:

```
        H        H        H        |
    H—C—      —C—      —C—      —C—
        H        H        |        |
Type:   1        2        3        4
```
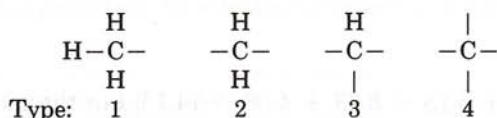
Paraffinic hydrocarbons	ΔC
Base group, methane	0.73
First methyl substitution	2.00
Second methyl substitution	3.18
Third methyl substitution	3.68
Fourth and successive methyl substitutions	4.56

For example, C for n-octane is equal to $[0.73 + 2.00 + 3.18 + 3.68 + 4(4.56)] = 27.8$

Isoparaffins are formed by determining the C for the paraffin with the longest possible straight-chain carbon backbone and then making successive substitutions of hydrogen atoms by methyl groups. Values of ΔC

attributable to such substitutions are shown below:

Type of substitution	ΔC
$1 \leftarrow 2 \rightarrow 1$	3.64
$1 \leftarrow 2 \rightarrow 2$	4.71
$1 \leftarrow 2 \rightarrow 3$	5.79
$2 \leftarrow 2 \rightarrow 2$	5.79
$1 \leftarrow 3 \rightarrow 1$ $\downarrow$ 1	3.39
$1 \leftarrow 3 \rightarrow 1$ $\downarrow$ 2	4.50
$1 \leftarrow 3 \rightarrow 1$ $\downarrow$ 3	5.61

The type of carbon atom from which the arrow points away is the one involved in the methyl substitution. The arrows point toward the types of adjacent atoms. To calculate C for an isoparaffin, beginning with the longest chain, introduce side chains beginning with the left end and proceed in a clockwise direction. To illustrate with 2,2,4-trimethylpentane,
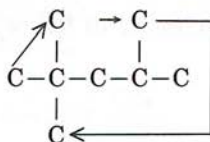
n-Pentane $= 0.73 + 2.00 + 3.18 + 3.68 + 4.56 = 14.15$. For the methyl substitutions

$$1 \leftarrow 2 \rightarrow 2 = 4.71; \quad 2 \leftarrow 2 \rightarrow 1 = 4.71; \quad \text{and} \quad 1 \leftarrow 3 \rightarrow 2 = 4.50$$
$$\downarrow$$
$$1$$

Thus, $\qquad C = 14.15 + 4.71 + 4.71 + 4.50 = 28.07.$

Olefinic and acetylenic hydrocarbons. First determine C for the corresponding saturated hydrocarbon, as described above; then insert the unsaturated bond(s) and employ the following ΔC contributions:

		ΔC
First double bond	$1 \leftrightarrow 1$	-1.19
	$1 \leftrightarrow 2$	-0.65
	$2 \leftrightarrow 2$	-0.29
Second double bond	$2 \leftrightarrow 1$	-0.17
Any acetylenic bond		-0.83

Naphthenes. Form the paraffinic hydrocarbon with the same number of carbon atoms as in the naphthene ring. Remove two terminal hydrogens and close the ring. $\Delta C = -1.0$.

Aromatics. Benzene has a C value of 13.2. Methyl-substituted benzenes have C values of $13.2 - (5.28)$ (number of methyl substitutions).

Before discussing the estimation of C for nonhydrocarbons, it is important to note that the simple rules shown above are incomplete and do not cover many types of hydrocarbons. There are, however, no experimental data that can be used to obtain additional ΔC contributions. In fact, some of the ΔC values quoted above are based on so few data that they should be considered only approximate. For the 27 *hydrocarbons* studied by Roy and Thodos, one can obtain a rough, but often satisfactory, correlation by using only molecular weight as the correlating parameter, i.e.,

$$C \approx 5.21 \times 10^{-2} M + 1.82 \times 10^{-3} M^2 \qquad M < 120 \qquad (10\text{-}3.16)$$

with M in g/mol and C dimensionless.

For *nonhydrocarbons,* C is again estimated by a group contribution method wherein one mentally synthesizes the final compound by a particular set of rules and employs ΔC values for each step.

Alcohols. Synthesize the corresponding hydrocarbon with the same carbon structure and calculate C as noted above. Replace the appropriate hydrogen atom by a hydroxyl group and correct C as noted:

Type of $-OH$ substitution	ΔC
On methane	3.79
$1 \leftarrow 1$	4.62
$2 \leftarrow 1$	4.11
$3 \leftarrow 1$	3.55
$4 \leftarrow 1$	3.03
$1 \leftarrow 2 \rightarrow 1$	4.12

The notation is the same as that used earlier; for example, $3 \leftarrow 1$ indicates that the $-OH$ group is replacing a hydrogen atom on a type 1 carbon which is adjacent to a type 3 carbon:

$$
\begin{array}{ccccccc}
\text{C} & & & & \text{C} & & \\
| & & & & | & & \\
\text{C} - \text{C} - \text{C} - \text{C} - \text{H} & \rightarrow & \text{C} - \text{C} - \text{C} - \text{C} - \text{OH}
\end{array}
$$
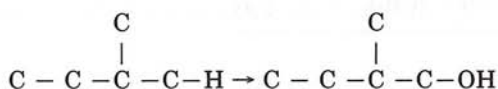
These rules apply only to aliphatic alcohols, and they are incomplete even for them.

Amines.   Estimation of C for amines is similar to that described above for alcohols. First, synthesize the corresponding hydrocarbon segment (with the most complex structure) that is finally to be attached to a nitrogen. For *primary* amines, replace the appropriate terminal hydrogen by a $-NH_2$ group with the following ΔC contributions:

Type of substitution	ΔC
On methane	2.60
$1 \leftarrow 1$	3.91
$1 \leftarrow 2 \rightarrow 1$	5.08
$2 \leftarrow 2 \rightarrow 1$	7.85
$1 \leftarrow 3 \rightarrow 1$	6.50
$\downarrow$	
1	

For *secondary* amines, there are additional ΔC values:

	ΔC
$CH_3 - NH_2 \rightarrow CH_3 -\overset{\overset{\text{H}}{\mid}}{N}- CH_3$	3.31
$- CH_2 - NH_2 \rightarrow - CH_2 -\underset{\underset{\text{H}}{\mid}}{N}- CH_3$	4.40

Finally, for *tertiary* amines, Roy and Thodos show three types of corrections applicable to the secondary amines:

	ΔC
$CH_3 - NH - CH_3 \rightarrow (CH_3)_3 \equiv N$	2.59
$- CH_2 - \overset{\overset{\text{H}}{\mid}}{N} - CH_2 - \rightarrow -CH_2 - \overset{\overset{\text{CH}_3}{\mid}}{N} - CH_2 -$	3.27
$- CH_2 - \overset{\overset{\text{H}}{\mid}}{N} - CH_3 \rightarrow - CH_2 - N - (CH_3)_2$	2.94

After calculating C for an amine as noted above, any methyl substitutions for a hydrogen on a side chain increase C by 4.56 (the same as shown for fourth and successive methyl substitutions in paraffinic hydrocarbons).

For example,

$$-N-CH_3 \rightarrow -N-CH_2-CH_3 \quad \Delta C = 4.56$$
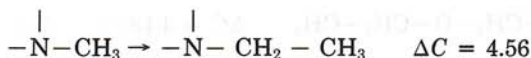
Nitriles. Only three ΔC contributions are shown; they were based on thermal conductivity data for acetonitrile, propionitrile, and acrylic nitrile.

Type of $-CN$ addition	ΔC
On methane	5.43
$CH_3-CH_3 \rightarrow CH_3-CH_2-CN$	7.12
$-CH=CH_2 \rightarrow -CH=CH-CN$	6.29

Halides. Suggested contributions are shown below; the order of substitution should be F, Cl, Br, I.

	ΔC
First halogen substitution on methane:	
Fluorine	0.26
Chlorine	1.38
Bromine	1.56
Iodine	2.70
Second and successive substitutions on methane:	
Fluorine	0.38
Chlorine	2.05
Bromine	2.81
Substitutions on ethane and higher hydrocarbons:	
Fluorine	0.58
Chlorine	2.93

Aldehydes and ketones. Synthesize the hydrocarbon analog with the same number of carbon atoms and calculate C as noted above. Then form the desired aldehyde or ketone by substituting oxygen for two hydrogen atoms:

	ΔC
$-CH_2-CH_3 \rightarrow -CH_2-CHO$	1.93
$-CH_2-CH_2-CH_2- \rightarrow -CH_2-CO-CH_2-$	2.80

Ethers. Synthesize the primary alcohol with the longest carbon chain on one side of the ether oxygen. Convert this alcohol to a methyl ether.

$$-CH_2OH \rightarrow -CH_2-O-CH_3 \quad \Delta C = 2.46$$
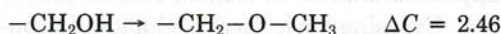
Extend the methyl chain, if desired, to an ethyl.

$$-CH_2-O-CH_3 \rightarrow -CH_2-O-CH_2-CH_3 \quad \Delta C = 4.18$$
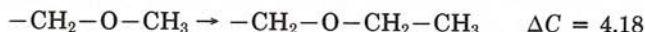
Although Roy and Thodos do not propose extensions beyond the ethyl group, presumably more complex chains could be synthesized by using ΔC values obtained from paraffinic and isoparaffinic contributions.

Acids and esters. Synthesize the appropriate ether so as to allow the following substitutions:

	ΔC
$-CH_2-O-CH_3 \rightarrow -CH_2-O-\underset{\underset{H}{\mid}}{C}= O$	0.75
$-CH_2-O-CH_2- \rightarrow -CH_2-O-\underset{\mid}{C}= O$	0.31

Cyclics. Synthesize the ring, if possible, with the following contributions (not substitutions):

Group	ΔC
$-CH_2-$	4.25
$-CH=$	3.50
$-NH-$	4.82
$-N=$	3.50
$-O-$	3.61
$=S=$	7.01

and determine C as:

$$C = \Sigma\ \Delta C - 7.83$$

The Roy and Thodos group contributions were obtained from limited data and are averaged values. Calculations cannot be made for many compounds by using the rules given above, but an intelligent guess for a missing increment can often be made. The Roy-Thodos method can also be used in a different way. If a single value of λ is available at a known temperature, Eq. (10-3.13) can be used with Table 10-1 to yield a value of C that can then be employed to determine λ at other temperatures.

Method of Chung et al. [27, 28]

Chung et al. employed an approach similar to that of Mason and Monchick to obtain a relation for λ. By using their form and a similar one for

low-pressure viscosity [Eq. (9-4.9)], one obtains

$$\frac{\lambda M'}{\eta C_v} = \frac{3.75\Psi}{C_v/R} \tag{10-3.17}$$

where λ = thermal conductivity, W/(m·K)
$\quad\ M'$ = molecular weight, kg/mol
$\quad\ \eta$ = low-pressure gas viscosity, N·s/m^2
$\quad\ C_v$ = heat capacity at constant volume, J/(mol·K)
$\quad\ R$ = gas constant, 8.314 J/(mol·K)
$\quad\ \Psi = 1 + \alpha\,\{[0.215 + 0.28288\alpha - 1.061\beta + 0.26665Z]/[0.6366 + \beta Z + 1.061\alpha\beta]\}$
$\quad\ \alpha = (C_v/R) - \frac{3}{2}$
$\quad\ \beta = 0.7862 - 0.7109\omega + 1.3168\omega^2$
$\quad\ Z = 2.0 + 10.5T_r^2$

The β term is an empirical correlation for $(f_{\text{int}})^{-1}$ [Eq. (10-3.4)] and is said to apply only for nonpolar materials. For polar materials, β is specific for each compound; Chung et al. [28] list values for a few materials. If the compound is polar and β is not available, use a default value of $(1.32)^{-1} = 0.758$.

Z has the same meaning as Z_{rot} in the Mason and Monchick analysis. For large values of Z, Ψ reduces to

$$\Psi = 1 + 0.2665\frac{\alpha}{\beta} \qquad \text{large } Z \tag{10-3.18}$$

If Eq. (10-3.18) is used in Eq. (10-3.17), the Eucken correlation [Eq. (10-3.3)] is obtained when β is set equal to unity. If $\beta = (1.32)^{-1}$, the modified Eucken relation [Eq. (10-3.5)] is recovered. The method is illustrated in Example 10-1.

Method of Ely and Hanley [40, 51]

An extended corresponding states procedure, the method of Ely and Hanley was developed to estimate the viscosities and thermal conductivities of nonpolar fluids, pure or mixtures, over a wide range of densities and temperatures. As illustrated in this section, the procedure has been simplified to treat the thermal conductivity of low-pressure, pure gases. Later we shall extend the approach to handle fluids at high densities. The estimation technique is based on Eucken's proposal to separate the thermal conductivity into contributions from the interchanges of both translational and internal energy. For the latter, the modified Eucken representation [in Eq. (10-3.5)] was used, but, for the translational component, a corresponding states method using methane as the reference component

was selected. Thus, with Eq. (10-3.2), with $f_{int} = 1.32$, we have

$$\frac{\lambda M'}{\eta^* C_v} = \frac{\lambda^* M'}{\eta^* C_v} + 1.32\left(1 - \frac{3/2}{C_v/R}\right) \tag{10-3.19}$$

In the application of Eq. (10-3.2), as noted earlier, the low-pressure, pure gas viscosity η was required as an input variable. In the Ely and Hanley method, η^* has the same connotation, but it is calculated as a part of the estimation procedure (as shown below). Equation (10-3.19) can be written as

$$\lambda = \lambda^* + \frac{\eta^*}{M'}(1.32)\left(C_v - \frac{3R}{2}\right) \tag{10-3.20}$$

where λ = thermal conductivity of the low-pressure gas, W/(m·K)
  M' = molecular weight, kg/mol
  C_v = heat capacity of the low-pressure gas at constant volume, J/(mol·K)
  R = 8.314 J/(mol·K)

λ^* and η^* are defined below. The calculational procedure is as follows:

1. Determine the reduced temperature $T_r = T/T_c$; then define a parameter T^+ such that

$$T^+ = T_r, \quad T_r \leq 2 \quad \text{or} \quad T^+ = 2 \quad T_r > 2 \tag{10-3.21}$$

2. Calculate the compound *shape* factors [78] relative to methane.

$$\theta = 1 + (\omega - 0.011)\left(0.56553 - 0.86276 \ln T^+ - \frac{0.69852}{T^+}\right) \tag{10-3.22}$$

$$\Phi = [1 + (\omega - 0.011)(0.38560 - 1.1617 \ln T^+)]\frac{0.288}{Z_c} \tag{10-3.23}$$

where the values 0.011 and 0.288 represent the acentric factor and critical compressibility factor of the reference fluid methane.

3. The shape factors are then used to compute scaling parameters for temperature and volume,

$$f = \frac{T_c}{190.4}\theta \tag{10-3.24}$$

$$h = \frac{V_c}{99.2}\Phi \tag{10-3.25}$$

with 190.4 the critical temperature of methane in kelvins and 99.2 the critical volume of methane in cm³/mol.

4. The temperature scaling parameter f is then used to determine the *equivalent* temperature T_0 to estimate the thermal conductivity and viscosity of the methane reference fluid at low pressure.

$$T_0 = \frac{T}{f} \tag{10-3.26}$$

$$\eta_0 = 10^{-7} \sum_{n=1}^{9} C_n T_0^{(n-4)/3} \tag{10-3.27}$$

$$\lambda_0 = 1944\eta_0\dagger \tag{10-3.28}$$

where η_0 is the low-pressure methane gas viscosity at T_0 $(\text{N}\cdot\text{s/m}^2)$ and λ_0 is the low-pressure methane gas thermal conductivity $[\text{W/(m}\cdot\text{K)}]$. The coefficients C_n for the series in Eq. (10-3.27) are:

$C_1 = 2.90774\ E+6$	$C_4 = -4.33190\ E+5$	$C_7 = 4.32517\ E+2$
$C_2 = -3.31287\ E+6$	$C_5 = 7.06248\ E+4$	$C_8 = -1.44591\ E+1$
$C_3 = 1.60810\ E+6$	$C_6 = -7.11662\ E+3$	$C_9 = 2.03712\ E-1$

5. To obtain λ^* and η^* in Eq. (10-3.20),

$$\lambda^* = \lambda_0 H \tag{10-3.29}$$

$$\eta^* = \eta_0 H \frac{M'}{16.04 \times 10^{-3}} \tag{10-3.30}$$

$$H = \left(\frac{16.04 \times 10^{-3}}{M'}\right)^{1/2} f^{1/2}/h^{2/3} \tag{10-3.31}$$

Thus, to use the Ely and Hanley method to estimate the thermal conductivity of low-pressure pure gases as a function of temperature, one needs the critical properties T_c, V_c, and Z_c as well as the acentric factor, molecular weight, and C_v at low pressure. Some calculated values are compared with experimental data in Table 10-2, and the procedure is illustrated in Example 10-1.

Example 10-1 Estimate the thermal conductivity of 2-methylbutane (isopentane) vapor at 1 bar and 100°C. The reported value is 2.2×10^{-2} W/(m·K) [11].

solution From Appendix A, $T_c = 460.4$ K, $P_c = 33.4$ bar, $V_c = 306$ cm^3/mol, $Z_c = 0.267$, $\omega = 0.227$, and $M = 72.151$ g/mol $= 72.151 \times 10^{-3}$ kg/mol.

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†The coefficient 1944 is obtained by considering the first term of Eq. (10-3.2) after cross-multiplying by $\eta_0 C_v/M'$, that is, the term is then $\frac{15}{4}(R/M')\eta_0$. With $R = 8.314$ J/(mol·K) and M' for methane as 16.04×10^{-3}, we have $1944\eta_0$, where η_0 is in N·s/m^2.

TABLE 10-2 Comparison between Calculated and Experimental Values of the Thermal Conductivity of a Pure Gas at 1 bar

Compound	T, K	λ, exp. W/(m·K) × 10³	η N·s/m² × 10⁷	C_v, J/(mol·K)	Ref.	Eucken factor	Percent Error†					
							Eucken	Mod. Eucken	Stiel and Thodos	Roy and Thodos	Chung et al.	Ely and Hanley
Acetaldehyde† $M' = 44.05 \times 10^{-3}$	313	12.6	91.0	48.2	176	1.27	8.6	27	17	7.5	8.1	14
	353	15.9	103	52.3		1.30	4.4	23	13	3.9	6.4	10
	393	19.4	115	56.5		1.32	1.2	20	10	1.6	5.3	8.8
Acetone† $M' = 58.08 \times 10^{-3}$	353	15.7	90.0	77.9	176	1.30	−4.7	16	5.1	2.9	0	−0.6
	393	19.4	100	84.2		1.34	−8.7	12	0.9	1.2	−2.3	−3.1
	457	24.7	114.5	96.1	17	1.29	−8.4	13	1.7	4.5	0.8	1.6
Acetonitrile† $M' = 41.05 \times 10^{-3}$	353	12.4	85	49.0	176	1.22	13	33	22	2.7	12	−8.1
	393	15.0	95	52.6		1.23	10	30	19	2.9	11	−9.3
Acetylene $M' = 26.04 \times 10^{-3}$	198	11.8	70.1	26.8	17	1.64	3.8	14	8.8	10	3.0	5.1
	273	18.7	95.5	33.7		1.51	2.8	16	9.1	5.7	8.3	10
	373	29.8	126.1	40.4		1.52	−4.0	10	2.9	1.9	7.0	11
Ammonia† $M' = 17.03 \times 10^{-3}$	213	16.5	73.2	25.4	17	1.51	15	26	20		7.3	−1.2
	273	21.9	90.6	26.7		1.54	10	21	16		6.6	1.4
Benzene $M' = 78.11 \times 10^{-3}$	353	14.6	90	90.4	176	1.40	−14	5.8	−4.6	1.0	−1.7	−2.1
	433	22.6	109.5	114		1.41	−18	2.5	−8.2	0	−1.6	−2.7
n-Butane $M' = 58.12 \times 10^{-3}$	273	13.5	68.8	84.6	39	1.35	−9.4	11	0.1	−2.0	2.3	5.2
	373	24.6	94.5	110		1.38	−15	5.7	−5.2	−3.7	1.5	1.6
Carbon dioxide $M' = 44.01 \times 10^{-3}$	200	9.51	101.5	24.7	17	1.67	5.3	15	9.8		4.9	6.2
	300	16.7	149.5	28.9		1.70	−3.2	7.5	1.9		2.8	5.4
	473	28.4	225.0	35.6		1.56	−2.2	11	4.1		11	20
	598	37.9	272.8	39.5		1.55	−4.8	9.3	1.9		11	25
	1273	81.7	465.1	48.8		1.58	−13	2.4	−5.6		7.3	20

Carbon tetrachloride	273	5.95	91.0	72.4	17	1.39	−9.4	9.7	−0.4	−9.6	−2.4	2.9
$M' = 153.82 \times 10^{-3}$	373	8.58	124.3	81.7		1.30	−5.4	15	4.4	5.6	6.3	11
	457	10.9	151.2	86.3		1.28	−5.3	16	4.7	17	9.4	15
Cyclohexane	353	16.3	83.0	123	176	1.34	−14	7.1	−4.2	−0.6	2.6	0
$M' = 84.16 \times 10^{-3}$	433	25.6	100.5	155		1.38	−19	2.3	−9.0	−1.0	0.5	−2.0
Dichlorodifluoromethane	273	8.29	114.2	57.8	17	1.52	−12	4.3	−4.5	0.7	−5.6	0.5
$M' = 120.21 \times 10^{-3}$	373	13.8	155.1	69.1		1.56	−18	−1.0	−9.9	−0.4	−6.4	−1.5
	473	19.4	193.6	77.1		1.57	−20	−3.3	−12	3.8	−5.8	−0.5
Ethyl acetate‡	319	12.1	81.1	105	17	1.24	−5.9	17	4.7	6.9	1.3	−0.8
$M' = 88.11 \times 10^{-3}$	373	16.2	95.5	121		1.24	−6.5	17	4.4	7.3	3.4	0.6
	457	23.8	116	142		1.27	−11	12	−0.3	8.4	1.3	0
Ethyl alcohol‡	293	15.0	84.8	56.5	17	1.44	−7.7	9.6	0.4	−2.9	−8.8	−25
$M' = 46.07 \times 10^{-3}$	401	24.9	116.6	72.4		1.36	−7.4	12	1.8	−1.5	−2.5	−18
Ethylene	273	17.4	94.2	32.8	17	1.58	−0.6	12	5.4	−0.3	3.3	8.0
$M' = 28.05 \times 10^{-3}$	373	27.8	124.5	43.1		1.46	−1.3	14	6.1	3.0	8.3	14
Ethyl ether	273	13.0	68.4	104	176	1.35	−13	7.9	−3.1	−3.2	1.8	−5.4
$M' = 74.12 \times 10^{-3}$	373	22.2	93.7	121		1.45	−20	−0.7	−11	2.5	−3.6	−9.9
	486	35.1	120.8	148		1.45	−23	−2.5	−13	8.2	−2.6	−7.4
n-Hexane	373	20.1	79.0	163	176	1.34	−17	4.8	−6.8	−0.8	3.4	−2.5
$M' = 86.18 \times 10^{-3}$	433	27.2	92.0	186		1.37	−20	2.1	−9.4	−1.2	2.1	−3.7
Isopropyl alcohol‡	304	15.2	78.5	75.4	17	1.54	−19	−1.8	−11	−6.6	−17	−29
$M' = 60.10 \times 10^{-3}$	400	25.0	105.6	101		1.41	−16	4.0	−6.5	−8.8	8.1	−22
Sulfur dioxide	273	8.29	117	30.6	17	1.48	8.6	21	15	9.0	9.0	11
$M' = 64.06 \times 10^{-3}$												

†Percent error = [(calc. − exp.)/exp.] × 100

‡Compounds for which β was set equal to $(1.32)^{-1}$ as a default value in the Chung et al. method.

First we need to estimate the viscosity of 2-methylbutane. Using the Chung et al. correlation, Eq. (9-4.9),

$$\eta = \frac{40.785 F_c \, (MT)^{1/2}}{V_c^{2/3} \Omega_v}$$

where $F_c = 1 - 0.275\omega$, since μ_r and $\kappa = 0$, $T^* = 1.2593 \, T_r = 1.2593[(100 + 273)/460.4] = 1.020$, and $\Omega = 1.576$ from Eq. (9-4.3). Thus,

$$\eta = \frac{(40.785) \, [1 - (0.275) \, (0.227)] \, [(72.151) \, (373)]^{1/2}}{(306)^{2/3} \, (1.576)}$$

$$= 87.7 \, \mu P = 8.77 \times 10^{-5} \, P = 8.77 \times 10^{-6} \, N \cdot s/m^2$$

The ideal-gas value of C_v is estimated from $(C_p - R)$, where C_p is determined from the polynomial constants in Appendix A,

$$C_p = -9.525 + (0.5066) \, (373) - (2.729 \times 10^{-4}) \, (373)^2 + (5.723 \times 10^{-8}) \, (373)^3$$

$$= 144.2 \, J/(mol \cdot K)$$

$$C_v = 144.2 - 8.3 = 135.9 \, J/(mol \cdot K)$$

$$M' = 72.151 \times 10^{-3} \, kg/mol$$

EUCKEN METHOD, Eq. (10-3.3)

$$\lambda = \frac{\eta C_v}{M'} \left(1 + \frac{9/4}{C_v/R} \right)$$

$$= \frac{(8.77 \times 10^{-6}) \, (135.9)}{72.151 \times 10^{-3}} \left[1 + \frac{9/4}{135.9/8.314} \right]$$

$$= 1.88 \times 10^{-2} \, W/(m \cdot K)$$

$$\text{Error} = \frac{1.88 - 2.2}{2.2} \times 100 = -14\%$$

MODIFIED EUCKEN METHOD, Eq. (10-3.5)

$$\lambda = \frac{\eta C_v}{M'} \left(1.32 + \frac{1.77}{C_v/R} \right)$$

$$= \frac{(8.77 \times 10^{-6}) \, (135.9)}{72.151 \times 10^{-3}} \left(1.32 + \frac{1.77}{135.9/8.314} \right)$$

$$= 2.36 \times 10^{-2} \, W/(m \cdot K)$$

$$\text{Error} = \frac{2.36 - 2.2}{2.2} \times 100 = 7.2\%$$

STIEL AND THODOS METHOD, Eq. (10-3.6)

$$\lambda = \frac{\eta C_v}{M'} \left(1.15 + \frac{2.03}{C_v/R} \right)$$

$$= \frac{(8.77 \times 10^{-6}) \, (135.9)}{72.151 \times 10^{-3}} \left(1.15 + \frac{2.03}{135.9/8.314} \right)$$

$$= 2.11 \times 10^{-2} \, W/(m \cdot K)$$

$$\text{Error} = \frac{2.11 - 2.2}{2.2} \times 100 = -4.1\%$$

ROY-THODOS METHOD, Eq. (10-3.13)

$$\lambda\Gamma = (\lambda\Gamma)_{tr} + (\lambda\Gamma)_{int}$$

Γ is defined in Eq. (10-3.12),

$$\Gamma = 210 \left(\frac{T_c M^3}{P_c^4} \right)^{1/6}$$

$$= 210 \left[\frac{(460.4) \, (72.151)^3}{(33.4)^4} \right]^{1/6} = 478$$

With a reduced temperature, $T_r = (100 + 273)/460.8 = 0.810$, $(\lambda\Gamma)_{tr}$ is found from Eq. (10-3.14),

$$(\lambda\Gamma)_{tr} = 8.757\{\exp[(0.0464)(0.810)] - \exp[(-0.2412)(0.810)]\} = 1.89$$

To find $(\lambda\Gamma)_{int}$, C must first be determined by synthesizing n-butane with the recommended ΔC increments.

$$n\text{-butane} = (0.73 + 2.00 + 3.18 + 3.68) = 9.59$$

Next, to form 2-methylbutane, a $1{\leftarrow}2{\rightarrow}2$ methyl substitution is required. Thus,

$$C \text{ (2-methylbutane)} = 9.59 + 4.71 = 14.30$$

The appropriate $f(T_r)$ is given in Table 10-1 for saturated hydrocarbons,

$$f(T_r) = -0.152T_r + 1.191T_r^2 - 0.039T_r^3$$

$$= (-0.152)(0.810) + (1.191)(0.810)^2 - (0.039)(0.810)^3 = 0.638$$

Then,

$$(\lambda\Gamma)_{int} = Cf(T_r) = (14.30)(0.638) = 9.12$$

$$\lambda = \frac{1.89 + 9.12}{478} = 2.30 \times 10^{-2} \text{ W/(m·K)}$$

$$\text{Error} = \frac{2.30 - 2.2}{2.2} \times 100 = 4.5\%$$

CHUNG ET AL. METHOD, Eq. (10-3.17)

$$\frac{\lambda M'}{\eta C_v} = \frac{3.75\Psi}{C_v/R}$$

As defined under Eq. (10-3.17),

$$\alpha = \frac{C_v}{R} - 1.5 = \frac{135.9}{8.314} - 1.5 = 14.85$$

$$\beta = 0.7862 - (0.7109)(0.227) + (1.3168)(0.227)^2 = 0.693$$

$$T_r = \frac{373}{460.4} = 0.810 \text{ and } Z = 2.0 + (10.5)(0.810)^2 = 8.89$$

$$\Psi = 1 + 14.85 \, \frac{0.215 + (0.28288)(14.85) - (1.061)(0.693) + (0.26665)(8.89)}{0.6366 + (0.693)(8.89) + (1.061)(14.85)(0.693)}$$

$$= 6.073$$

$$\lambda = \frac{(3.75)(6.073)}{135.9/8.314} \frac{(8.77 \times 10^{-6})(135.9)}{72.151 \times 10^{-3}}$$

$$= 2.30 \times 10^{-2} \text{ W/(m·K)}$$

$$\text{Error} = \frac{2.30 - 2.2}{2.2} \times 100 = 4.5\%$$

ELY AND HANLEY METHOD, Eq. (10-3.20).   Following the steps outlined in the text:

1. $T_r = 373/460.4 = 0.810$; thus, $T^+ = T_r = 0.810$

2. $\Theta = 1 + (0.227 - 0.011)\left[0.56553 - 0.86276 \ln (0.810) - \dfrac{0.69852}{0.810}\right]$

    $= 0.97527$

    $\Phi = \{1 + (0.227 - 0.011)[0.38560 - 1.1627 \ln (0.810)]\}\dfrac{0.288}{0.267}$

    $= 1.2248$

3. $f = \dfrac{460.4}{190.4} 0.97527 = 2.356$

    $h = \dfrac{306}{99.2} 1.2248 = 3.778$

4. $T_0 = \dfrac{373}{2.356} = 158.3 \text{ K}$

    $\eta_0 = 10^{-7} \sum C_n (158.3)^{(n-4)/3} = 6.22 \times 10^{-6} \text{ N}\cdot\text{s/m}^2$

    $\lambda_0 = (1944)(6.22 \times 10^{-6}) = 1.21 \times 10^{-2} \text{ W/(m}\cdot\text{K)}$

5. $H = \left(\dfrac{16.04 \times 10^{-3}}{72.151 \times 10^{-3}}\right)^{1/2} \dfrac{(2.356)^{1/2}}{(3.778)^{2/3}} = 0.2984$

    $\eta^* = (6.22 \times 10^{-6})(0.2984)\dfrac{72.151 \times 10^{-3}}{16.04 \times 10^{-3}} = 8.35 \times 10^{-6} \text{ N}\cdot\text{s/m}^2$

    $\lambda^* = (1.21 \times 10^{-2})(0.2984) = 3.61 \times 10^{-3} \text{ W/(m}\cdot\text{K)}$

Then, with Eq. (10-3.20),

$$\lambda = 3.61 \times 10^{-3} + \dfrac{8.35 \times 10^{-6}}{72.151 \times 10^{-3}} (1.32)\left[135.9 - \dfrac{(3)(8.314)}{2}\right]$$

$$= 3.61 \times 10^{-3} + 1.89 \times 10^{-2} = 2.25 \times 10^{-2} \text{ W/(m}\cdot\text{K)}$$

$$\text{Error} = \dfrac{2.25 - 2.2}{2.2} \times 100 = 2.2\%$$

Example 10-2 Use the Roy-Thodos method to estimate the thermal conductivity of ethyl acetate at 184°C and 1 bar. The reported value is $2.38 \times 10^{-2} \text{ W/(m}\cdot\text{K)}$ [17].

solution From Appendix A, $T_c = 523.2 \text{ K}$, $P_c = 38.3 \text{ bar}$, and $M = 88.107 \text{ g/mol}$. From Eq. (10-3.12),

$$\Gamma = 210 (T_c M^3/P_c^4)^{1/6}$$

$$= 210\left[\dfrac{(523.2)(88.107)^3}{(38.3)^4}\right]^{1/6} = 493$$

With $T = 184 + 273 = 457 \text{ K}$, with $T_r = 457/523.2 = 0.873$, and using Eq. (10-3.14),

$$(\lambda\Gamma)_{tr} = 8.757 \{\exp [(0.0464)(0.873)] - \exp [(-0.2412)(0.873)]\} = 2.02$$

To determine C, the synthesis plan is as follows: ethane $\rightarrow$ ethanol $\rightarrow$ methyl ethyl ether $\rightarrow$ diethyl ether $\rightarrow$ ethyl acetate. For ethane, $C = 0.73 + 2.00 = 2.73$. Converting to ethanol, $\Delta C = 4.62$. Next, to make methyl ethyl ether, $\Delta C = 2.46$ and then on to diethyl ether, $\Delta C = 4.18$. Finally, we form the ester, ethyl acetate, $\Delta C = 0.31$. Summing, $C = 2.73 + 4.62 + 2.46 + 4.18 + 0.31 = 14.30$. With Table 10-1 for esters,

$$f(T_r) = -0.082 T_r + 1.045 T_r^2 + 0.037 T_r^3$$
$$= (-0.082)(0.873) + (1.045)(0.873)^2 + (0.037)(0.873)^3 = 0.750$$

Then, with Eq. (10-3.13),

$$\lambda_r = \lambda \Gamma = (\lambda \Gamma)_{tr} + (\lambda \Gamma)_{int} = 493 \lambda = 2.02 + (14.3)(0.750)$$
$$\lambda = 2.58 \times 10^{-2} \, W/(m \cdot K)$$
$$\text{Error} = \frac{2.58 - 2.38}{2.38} \times 100 = 8.4\%$$

Discussion

Except for the Roy-Thodos method, all other methods described in this section for estimating the thermal conductivity of a pure gas at ambient pressure correlate the Eucken factor $\lambda M'/\eta C_v$ as a function of other variables such as C_v, T_r, and ω. To use them, independent values of the gas viscosity and heat capacity are necessary, although the Ely-Hanley procedure estimates its own viscosity. The Roy-Thodos correlation requires only the critical temperature and pressure and employs a group contribution method to account for the effect of internal degrees of freedom. In Table 10-2, we show the percent errors found when applying all of these techniques to estimate λ for a variety of compounds. As noted earlier, the Eucken equation (10-3.3) tends to underestimate λ, whereas the modified Eucken equation overestimates λ. The Stiel and Thodos equation yields λ values between the two Eucken forms. All three of these relations predict that the Eucken factor should decrease with temperature, whereas, in actuality, the factor appears, in most cases, to increase slightly (see Fig. 10-2). The Chung et al. and Ely-Hanley modifications do predict the correct trend of the Eucken factor with temperature and, except for polar compounds, yield λ values quite close to those reported experimentally. The Roy-Thodos method generally yields the smallest errors, but it is not applicable to inorganic compounds and, even for many types of organic compounds, group contributions are lacking.

It is recommended that, for *nonpolar* compounds, the Chung et al., the Ely-Hanley, or the Roy-Thodos method be used to estimate λ for pure gases at ambient pressure. Errors vary, but, generally, they do not exceed 5 to 7 percent. For *polar* compounds, the Roy-Thodos form is recommended. Other new estimation techniques for λ [37, 164] were found to be less accurate than the ones noted above.

10-4   Effect of Temperature on the Low-Pressure Thermal Conductivities of Gases

Thermal conductivities of low-pressure gases increase with temperature. The exact dependence of λ on T is difficult to judge from the λ-estimation methods in Sec. 10-3 because other temperature-dependent parameters (e.g., heat capacities and viscosities) are incorporated in the correlations. Generally, $d\lambda/dT$ ranges from 4×10^{-5} to 1.2×10^{-4} W/(m·K²), with the more complex and polar molecules having the larger values. Several power laws relating λ with T have been proposed [30, 107], but they are not particularly accurate. Miller et al. [101] have listed polynomial constants to estimate λ as a function of temperature for many gases, and they are shown in Table 10-3. To illustrate the trends, Fig. 10-4 has been drawn to show λ as a function of temperature for a few selected gases.

10-5   Effect of Pressure on the Thermal Conductivities of Gases

The thermal conductivities of all gases increase with pressure, although the effect is relatively small at low and moderate pressures. Three pressure regions in which the effect of pressure is distinctly different are discussed below.

Very low pressure

Below pressures of about 10^{-3} bar, the mean free path of the molecules is large compared to typical dimensions of a measuring cell, and there λ is almost proportional to pressure. This region is called the *Knudsen domain*. In reported thermal conductivity data, the term *zero-pressure value* is often used; however, it refers to values extrapolated from higher pressures (above 10^{-3} bar) and not to measured values in the very low pressure domain.

Low pressure

This region extends from approximately 10^{-3} to 10 bar and includes the domain discussed in Secs. 10-3 and 10-4. The thermal conductivity increases about 1 percent or less per bar [68, 174, 175, 176]. Such increases are often ignored in the literature, and either the 1-bar value or the "zero-pressure" extrapolated value may be referred to as the low-pressure conductivity.

TABLE 10-3 Thermal Conductivities of Some Gases at About 1 Bar[1]

$\lambda = A + BT + CT^2 + DT^3$; λ in W/(m·K) and T in kelvins

Formula	Name	A	B	C	D	λ(298 K)	Range
He	helium	3.722E-2	3.896E-4	-7.450E-8	1.290E-11	1.47E-1	115 to 1070
Ne	neon	9.108E-2	1.541E-4	-8.396E-8	2.530E-11	4.83E-2	115 to 1470
A	argon	2.714E-3	5.540E-5	-2.178E-8	5.528E-12	1.74E-2	115 to 1470
H2	hydrogen	8.099E-3	6.689E-4	-4.158E-7	1.562E-10	1.75E-1	115 to 1470
N2	nitrogen	3.919E-4	9.816E-5	-5.067E-8	1.504E-11	2.55E-2	115 to 1470
O2	oxygen	-3.273E-4	9.966E-5	-3.743E-8	9.732E-12	2.63E-2	115 to 1470
F2	fluorine	7.812E-4	8.287E-5	5.193E-8	-7.441E-11	2.81E-2	145 to 795
Cl2	chlorine	1.361E-3	2.429E-5	8.794E-9	-5.235E-12	9.24E-3	195 to 1470
Br2	bromine	-6.700E-5	1.729E-5	-1.256E-9	-3.769E-13	4.97E-3	195 to 1470
I2	iodine	2.638E-4	1.143E-5	-1.256E-9	6.281E-13	3.58E-3	195 to 1470
HF	hydrogen fluoride	3.857E-3	5.276E-5	2.261E-9	-9.841E-13	2.13E-2	175 to 1670
HCl	hydrogen chloride	-1.089E-4	5.306E-5	-1.047E-8	6.700E-13	1.48E-2	125 to 1670
HBr	hydrogen bromide	-7.915E-4	3.836E-5	-1.089E-8	2.219E-12	9.73E-3	125 to 1670
HI	hydrogen iodide	-2.152E-3	3.049E-5	-9.213E-9	1.801E-12	6.16E-3	125 to 1670
CO	carbon monoxide	5.067E-4	9.125E-5	-3.524E-8	8.199E-12	2.48E-2	115 to 1670
CO2	carbon dioxide	-7.215E-3	8.015E-5	5.477E-9	-1.053E-11	1.69E-2	185 to 1670
SO2	sulfur dioxide	-8.086E-3	6.344E-5	-1.382E-8	2.303E-12	9.65E-3	273 to 1670
SO3	sulfur trioxide	-6.683E-3	7.077E-5	-1.968E-8	1.256E-11	1.30E-2	175 to 1270
N2O	nitrous oxide	-7.835E-3	8.903E-5	-8.970E-9	-2.668E-12	1.78E-2	175 to 1670
NO	nitric oxide	5.021E-3	7.194E-5	-0.838E-9	-3.559E-12	2.63E-2	85 to 1670
NO2	nitrogen dioxide	-1.404E-2	1.108E-4	-3.162E-8	4.485E-12	1.63E-2	300 to 1670
H2O	water	7.341E-3	-1.013E-5	1.801E-7	-9.100E-11	1.79E-2	273 to 1070
H2O2	hydrogen peroxide	-8.823E-3	7.106E-5	7.119E-9	-6.533E-12	1.28E-2	273 to 1470
NH3	ammonia	3.811E-4	5.389E-5	1.227E-7	-3.635E-11	2.64E-2	273 to 1670
N2H4	hydrazine	-2.257E-2	1.193E-4	8.375E-9	-7.956E-13	1.37E-2	273 to 1670

TABLE 10-3 Thermal Conductivities of Some Gases at About 1 Bar *(Continued)*

$\lambda = A + BT + CT^2 + DT^3$; λ in W/mK and T in kelvins

Formula	Name	A	B	C	D	λ(298 K)	Range
CH_4	methane	-1.869E-3	8.727E-5	1.179E-7	-3.614E-11	3.37E-2	273 to 1270
C_2H_6	ethane	-3.174E-2	2.201E-4	-1.923E-7	1.664E-10	2.12E-2	273 to 1020
C_3H_8	propane	1.858E-3	-4.698E-6	2.177E-7	-8.409E-11	1.76E-2	273 to 1270
C_2H_4	ethylene	-1.760E-2	1.200E-4	3.335E-8	-1.366E-11	2.08E-2	200 to 1270
C_3H_6	propylene	-7.584E-3	6.101E-5	9.966E-8	-3.840E-11	1.84E-2	175 to 1270
C_4H_8	1-butene	-1.052E-2	5.771E-5	1.018E-7	-4.271E-11	1.46E-2	175 to 1270
C_4H_8	isobutylene	-2.776E-3	-2.806E-6	2.525E-7	-1.281E-10	1.54E-2	273 to 1070
C_4H_6	1,3-butadiene	-2.844E-2	1.255E-4	7.286E-8	-5.109E-11	1.41E-2	273 to 1270
C_5H_8	isoprene	-2.363E-2	1.101E-4	5.486E-8	-3.174E-11	1.32E-2	273 to 1270
C_6H_6	benzene	-8.455E-3	3.618E-5	9.799E-8	-4.058E-11	9.96E-3	273 to 1270
C_7H_8	toluene	7.596E-3	-4.008E-5	2.370E-7	-9.305E-11	1.42E-2	273 to 1270
C_8H_{10}	ethyl benzene	6.030E-4	-5.863E-6	2.140E-7	-8.924E-11	1.55E-2	273 to 1270
C_8H_{10}	o-xylene	-5.720E-3	3.572E-5	7.454E-8	-2.621E-11	1.09E-2	273 to 1270
C_8H_{10}	m-xylene	1.320E-2	-4.196E-5	1.662E-7	-6.106E-11	1.39E-2	273 to 1270
C_8H_{10}	p-xylene	-8.178E-3	3.890E-5	7.580E-8	-2.902E-11	9.38E-3	273 to 1270
C_8H_8	styrene	8.752E-4	-1.926E-6	1.244E-7	-5.071E-11	1.00E-2	273 to 1270
C_9H_{12}	cumene	-5.590E-3	2.253E-5	1.813E-7	-7.504E-11	1.52E-2	273 to 1270
$C_{10}H_8$	naphthalene	-9.380E-3	4.937E-5	3.811E-8	-1.064E-11	8.44E-3	273 to 1270
C_3H_6	cyclopropane	-8.568E-3	4.079E-5	1.579E-7	-6.817E-11	1.58E-2	273 to 1070
C_4H_8	cyclobutane	-9.795E-3	3.832E-5	1.474E-7	-6.202E-11	1.31E-2	273 to 1070
C_5H_{10}	cyclopentane	-8.522E-3	2.475E-5	1.621E-7	-6.914E-11	1.14E-2	273 to 1070
C_6H_{12}	cyclohexane	-8.614E-3	1.863E-5	1.704E-7	-7.249E-11	1.02E-2	273 to 1070
CH_3OH	methanol	-7.797E-3	4.167E-5	1.214E-7	-5.184E-11	1.40E-2	273 to 1270
C_2H_5OH	ethanol	-7.797E-3	4.167E-5	1.214E-7	-5.184E-11	1.40E-2	273 to 1270
C_3H_7OH	n-propanol	-7.931E-3	3.987E-5	1.193E-7	-5.021E-11	1.32E-2	273 to 1270
C_4H_9OH	n-butanol	-7.772E-3	3.564E-5	1.206E-7	-4.992E-11	1.22E-2	273 to 1270

$$\lambda = A + BT + CT^2 + DT^3; \quad \lambda \text{ in W/mK and } T \text{ in kelvins}$$

Formula	Name	A	B	C	D	λ(298 K)	Range
C2H4O	ethylene oxide	-1.459E-2	5.427E-5	1.520E-7	-7.647E-11	1.31E-2	273 to 1270
C3H7O	propylene oxide	-8.204E-3	3.664E-5	1.072E-7	-4.569E-11	1.10E-2	273 to 1270
C4H9O	butylene oxide	-9.150E-3	3.245E-5	9.883E-8	-4.464E-11	8.12E-3	273 to 1270
C6H5OH	phenol	-1.335E-2	6.390E-5	7.286E-8	-1.843E-11	1.17E-2	273 to 1270
C6H5NH2	aniline	-1.105E-2	4.979E-5	6.491E-8	-1.801E-11	9.07E-3	273 to 1270
CH3Cl	methyl chloride	-3.191E-3	1.579E-5	1.181E-7	-5.406E-11	1.06E-2	300 to 1270
CH2Cl2	methylene chloride	1.177E-3	-4.188E-6	9.673E-8	-4.276E-11	7.39E-3	300 to 1270
CHCl3	chloroform	-2.400E-3	2.634E-5	2.472E-8	-1.404E-11	7.27E-3	300 to 1270
CCl4	carbon tetrachloride	-1.742E-4	1.703E-5	2.561E-8	-1.493E-11	6.78E-3	300 to 1270
C6H5Cl	chlorobenzene	-6.394E-3	2.634E-5	7.328E-8	-2.316E-11	7.35E-3	273 to 1270
C4H5Cl	chloroprene	-1.142E-2	4.560E-5	1.189E-7	-5.507E-11	1.13E-2	273 to 1270

1. Miller, J.W. Jr., P.N. Shah, and C.L. Yaws, Chem. Eng. 83 (25), 153 (1976).
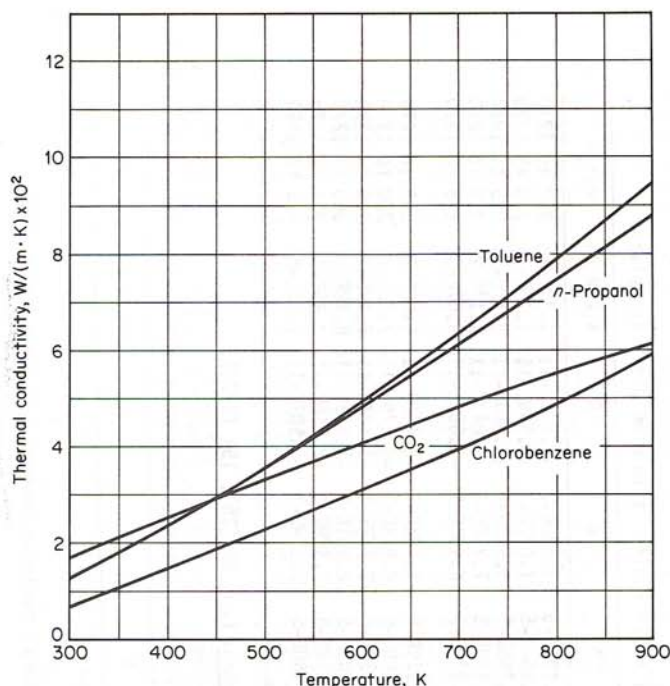
Figure 10-4 Effect of temperature on the thermal conductivity of some low-pressure gases.

High pressure

In Fig. 10-5 we show the thermal conductivity of propane over a wide range of pressures and temperatures [56]. The high-pressure gas domain would be represented by the curves on the right-hand side of the graph above the critical temperature (369.8 K). Increasing pressure raises the thermal conductivity, with the region around the critical point being particularly sensitive. Increasing temperature at low pressures results in a larger thermal conductivity, but at high pressure the opposite effect is noted. Similar behavior is shown for the region below T_c, where λ for liquids decreases with temperature whereas, for gases (see Sec. 10-4), there is an increase of λ with T. Pressure effects (except at very high pressures) are small below T_c. Not shown in Fig. 10-5 is the unusual behavior of λ near the critical point. In this region, the thermal conductivity is quite sensitive to both temperature and pressure [9]. Figure 10-6 shows a plot of λ for CO_2 near the critical point [50]. The explanation for this phenomenon is not clear; it may be due to a transition molecular ordering [73] or to small-scale circulation effects resulting from the migration of clusters of molecules [79]. In any case, when generalized charts of the effect of
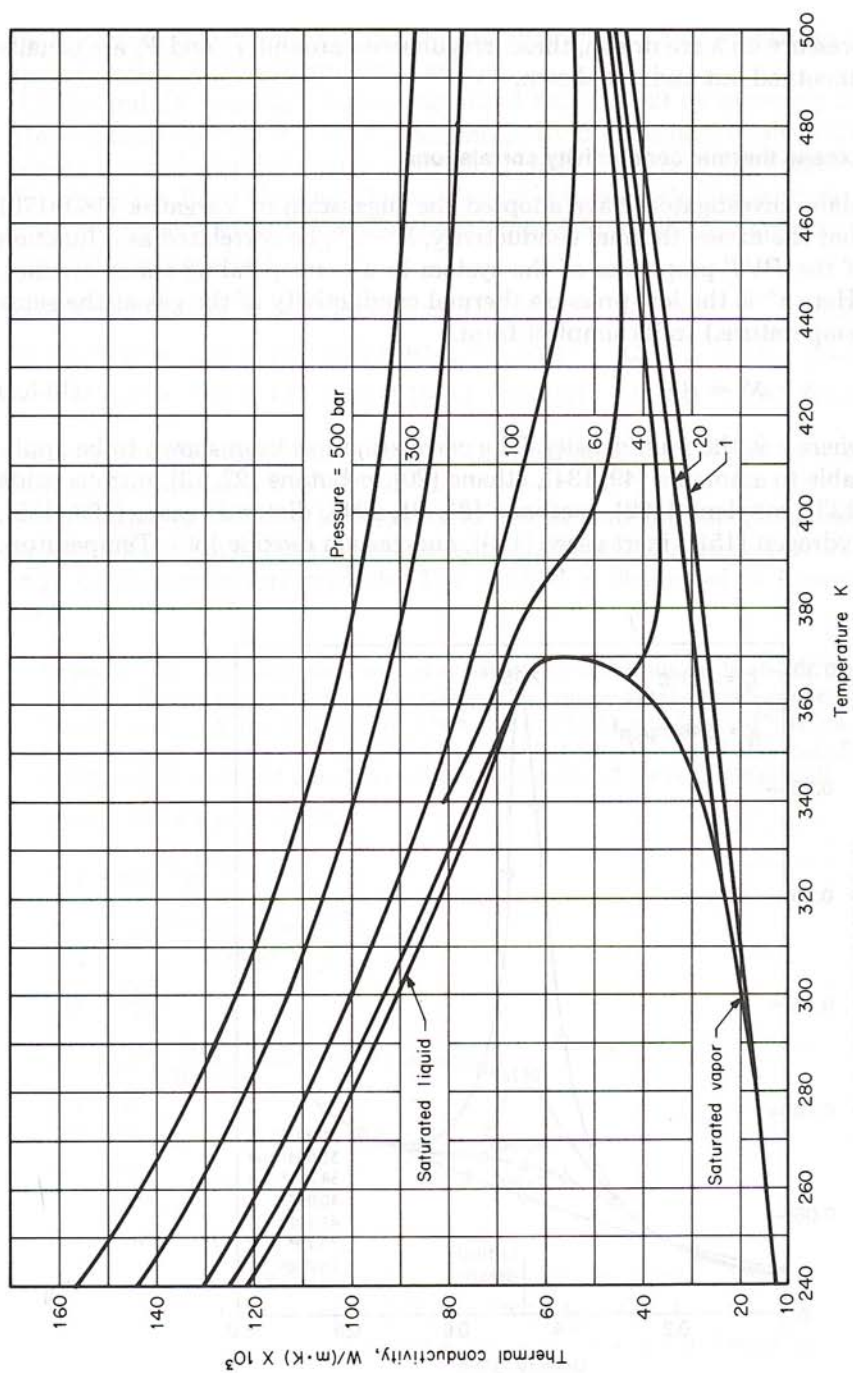
Figure 10-5 Thermal conductivity of propane. (*Data from Ref. 56.*)

pressure on λ are drawn, these irregularities around T_c and P_c are usually smoothed out and not shown.

Excess thermal conductivity correlations

Many investigators have adopted the suggestion of Vargaftik [169, 170] that the excess thermal conductivity, $\lambda - \lambda°$, be correlated as a function of the PVT properties of the system in a corresponding states manner. (Here $\lambda°$ is the low-pressure thermal conductivity of the gas at the same temperature.) In its simplest form,

$$\lambda - \lambda° = f(\rho) \tag{10-5.1}$$

where ρ is the fluid density. The correlation has been shown to be applicable to ammonia [49, 134], ethane [20], n-butane [22, 73], nitrous oxide [133], ethylene [122], methane [21, 91, 121], diatomic gases [103, 152], hydrogen [151], inert gases [120], and carbon dioxide [69]. Temperature
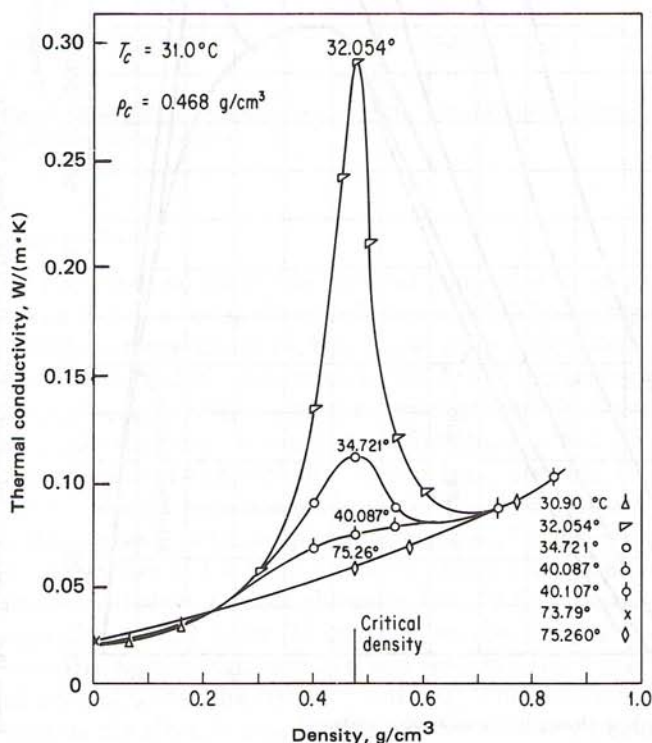
Figure 10-6 Thermal conductivity of carbon dioxide near the critical point. *(Data from Ref. 50.)*

and pressure do not enter explicitly, but their effects are included in the parameters $\lambda°$ (temperature only) and ρ.

Stiel and Thodos [157] have generalized Eq. (10-5.2) by assuming that $f(\rho)$ depends only on T_c, P_c, V_c, M, and ρ. By dimensional analysis they obtain a correlation between $\lambda - \lambda°$, Z_c, Γ, and ρ, where Γ was defined in Eq. (10-3.12). From data on 20 nonpolar substances, including inert gases, diatomic gases, CO_2, and hydrocarbons, they established the approximate analytical expressions:

$$(\lambda - \lambda°)\Gamma Z_c^5 = 1.22 \times 10^{-2} \left[\exp(0.535\rho_r) - 1\right] \qquad \rho_r < 0.5 \qquad (10\text{-}5.2)$$

$$(\lambda - \lambda°)\Gamma Z_c^5 = 1.14 \times 10^{-2} \left[\exp(0.67\rho_r) - 1.069\right] \qquad 0.5 < \rho_r < 2.0 \quad (10\text{-}5.3)$$

$$(\lambda - \lambda°)\Gamma Z_c^5 = 2.60 \times 10^{-3} \left[\exp(1.155\rho_r) + 2.016)\right] \qquad 2.0 < \rho_r < 2.8 \quad (10\text{-}5.4)$$

where λ is in W/(m·K), Z_c is the critical compressibility, and ρ_r is the reduced density $\rho/\rho_c = V_c/V$.

Equations (10-5.2) to (10-5.4) should not be used for polar substances or for hydrogen or helium. The general accuracy is in doubt, and errors of ± 10 to 20 percent are possible. The method is illustrated in Example 10-3.

Example 10-3 Estimate the thermal conductivity of nitrous oxide at 105°C and 138 bar. At this temperature and pressure, the experimental value is reported to be 3.90×10^{-2} W/(m·K) [133]. At 1 bar and 105°C, $\lambda° = 2.34 \times 10^{-2}$ W/(m·K) [133]. From Appendix A, $T_c = 309.6$ K, $P_c = 72.4$ bar, $V_c = 97.4$ cm³/mol, $Z_c = 0.274$, and $M = 44.013$ g/mol. At 105°C and 138 bar, Z for N_2O is 0.63 [32].

solution With Eq. (10-3.12),

$$\Gamma = 210 \left(\frac{T_c M^3}{P_c^4}\right)^{1/6}$$

$$= 210 \left[\frac{(309.6)(44.013)^3}{(72.4)^4}\right]^{1/6} = 209$$

$$V = \frac{ZRT}{P}$$

$$= \frac{(0.63)(8.314)(378)}{138 \times 10^5} \times 10^6 = 144 \text{ cm}^3/\text{mol}$$

$$\rho_r = \frac{V_c}{V}$$

$$= \frac{97.4}{144} = 0.676$$

Then, with Eq. (10-5.3),

$$(\lambda - \lambda°)(209)(0.274)^5 = (1.14 \times 10^{-2})\{\exp[(0.67)(0.676)] - 1.069\}$$

$$\lambda - \lambda° = 1.78 \times 10^{-2} \text{ W/(m·K)}$$

$$\lambda = (2.34 + 1.78) \times 10^{-2} = 4.12 \times 10^{-2} \text{ W/(m·K)}$$

$$\text{Error} = \frac{4.12 - 3.90}{3.90} \times 100 = 5.6\%$$

Method of Chung et al. [27, 28]

The low-pressure estimation procedure for pure component thermal conductivities developed by these authors, and given in Eq. (10-3.17), is modified to treat materials at high pressures (or densities).

$$\lambda = \frac{31.2\eta^{\circ}\Psi}{M'}(G_2^{-1} + B_6 y) + qB_7 y^2 T_r^{1/2} G_2 \qquad (10\text{-}5.5)$$

where λ = thermal conductivity, W/(m·K)
$\quad \eta^{\circ}$ = *low-pressure* gas viscosity, N·s/m^2
$\quad M'$ = molecular weight, kg/mol
$\quad \Psi = f(C_v, \omega, T_r)$ [as defined under Eq. (10-3.17)]
$\quad q = 3.586 \times 10^{-3}(T_c/M')^{1/2}/V_c^{2/3}$
$\quad T$ = temperature, K
$\quad T_c$ = critical temperature, K
$\quad T_r$ = reduced temperature, T/T_c
$\quad V_c$ = critical volume, cm^3/mol
$\quad y = \dfrac{V_c}{6V} \qquad\qquad\qquad\qquad\qquad\qquad\qquad (10\text{-}5.6)$

$$G_1 = \frac{1 - 0.5y}{(1 - y)^3} \qquad (10\text{-}5.7)$$

$$G_2 = \frac{(B_1/y)[1 - \exp(-B_4 y)] + B_2 G_1 \exp(B_5 y) + B_3 G_1}{B_1 B_4 + B_2 + B_3} \qquad (10\text{-}5.8)$$

The coefficients B_1 to B_7 are functions of the acentric factor ω, the reduced dipole moment μ_r [as defined in Eq. (9-4.11)], and the association factor κ. Some values of κ are shown in Table 9-1.

$$B_i = a_i + b_i \omega + c_i \mu_r^4 + d_i \kappa \qquad (10\text{-}5.9)$$

with a_i, b_i, c_i, and d_i given in Table 10-4.

The relation for high-pressure thermal conductivities is quite similar to

TABLE 10-4   Values of B_i in Eq. (10-5.9)
$B_i = a_i + b_i \omega + c_i \mu_r^4 + d_i \kappa$

i	a_i	b_i	c_i	d_i
1	2.4166 $E+0$	7.4824 $E-1$	$-9.1858\ E-1$	1.2172 $E+2$
2	$-5.0924\ E-1$	$-1.5094\ E+0$	$-4.9991\ E+1$	6.9983 $E+1$
3	6.6107 $E+0$	5.6207 $E+0$	6.4760 $E+1$	2.7039 $E+1$
4	1.4543 $E+1$	$-8.9139\ E+0$	$-5.6379\ E+0$	7.4344 $E+1$
5	7.9274 $E-1$	8.2019 $E-1$	$-6.9369\ E-1$	6.3173 $E+0$
6	$-5.8634\ E+0$	1.2801 $E+1$	9.5893 $E+0$	6.5529 $E+1$
7	9.1089 $E+1$	1.2811 $E+2$	$-5.4217\ E+1$	5.2381 $E+2$

the Chung et al. form for high-pressure viscosities [Eqs. (9-6.16) through (9-6.21)].

In Eq. (10-5.5), if V becomes large, y then approaches zero. In such a case, both G_1 and G_2 are essentially unity and Eq. (10-5.5) reduces to Eq. (10-3.17), the relation for λ at low pressures. To use Eq. (10-5.5), it should be noted that the viscosity $\eta°$ is for the *low-pressure*, pure gas. Experimental values may be employed or $\eta°$ can be estimated by the techniques given in Sec. 9-4. The dimensions of $\eta°$ are $N \cdot s/m^2$. The conversion from other viscosity units is $1\ N \cdot s/m^2 = 10\ P = 10^7\ \mu P$.

Chung et al. tested Eq. (10-5.5) with data from a large range of hydrocarbon types and from data for simple gases. Deviations over a wide pressure range were usually less than 5 to 8 percent. For highly polar materials, the correlation for β as given under Eq. (10-3.17) is not accurate and, at present no predictive technique to apply such compounds is available. [See the discussion dealing with polar materials under Eq. (10-3.17).]

The high-pressure Chung et al. method is illustrated in Example 10-4.

Method of Ely and Hanley [40, 51]

This estimation procedure was introduced in Sec. 10-3 for low-pressure, pure gases [Eq. (10-3.20)]. We now extend the treatment to cover pure components at high densities where Eq. (10-3.20) is modified to:

$$\lambda = \lambda^{**} + \frac{\eta^*}{M'}(1.32)\left(C_v - \frac{3R}{2}\right) \tag{10-5.10}$$

λ^{**} is defined below, and the second term in Eq. (10-5.10) is identical with that in Eq. (10-3.20) and is determined by the procedure outlined under that equation. It is not a function of the system density.

We adopt a calculational procedure similar to that shown in Sec. 10-3. The data required to estimate λ are T_c, V_c, Z_c, ω, M', C_v (at T and low pressure), T, and V. The dimensions of temperature and volume used here are kelvins and cm^3/mol. Z_c and ω have no dimensions, and M' and C_v are defined under Eq. (10-3.20).

1. Determine the reduced temperature and volume as $T_r = T/T_c$, $V_r = V/V_c$. Then define parameters T^+ and V^+ such that

$$
\begin{aligned}
T^+ &= T_r & T_r &\leq 2 & &(10\text{-}5.11)\\
&= 2 & T_r &> 2 \\
V^+ &= V_r & 0.5 &< V_r < 2 & &(10\text{-}5.12)\\
&= 0.5 & V_r &\leq 0.5 \\
&= 2 & V_r &\geq 2
\end{aligned}
$$

2. Calculate *shape* factors for the material relative to methane.

$$\theta = 1 + (\omega - 0.011)\,[0.09057 - 0.86276\ln T^+ \tag{10-5.13}$$
$$+ \left(0.31664 - \frac{0.46568}{T^+}\right)(V^+ - 0.5)]$$

$$\Phi = \{1 + (\omega - 0.011)\,[0.39490\,(V^+ - 1.02355) \tag{10-5.14}$$
$$- (0.93281)\,(V^+ - 0.75464)\ln T^+]\}\,\frac{0.288}{Z_c}$$

Note that, at low pressure, where V is large and, therefore, $V^+ = 2$, Eqs. (10-5.13) and (10-5.14) reduce to Eqs. (10-3.22) and (10-3.23).

3. Find the compound shape factors *relative* to methane,

$$f = \frac{T_c}{190.4}\,\theta \tag{10-5.15}$$

$$h = \frac{V_c}{99.2}\,\Phi \tag{10-5.16}$$

and use them to estimate the equivalent temperature T_0 and density ρ_0 to determine the thermal conductivity and viscosity of the methane chosen as the *reference fluid*.

$$T_0 = \frac{T}{f} \tag{10-5.17}$$

$$\rho_0 = \frac{16.04}{V}\,h \tag{10-5.18}$$

4. We now determine η_0, the low-pressure viscosity of the reference fluid (methane), with T_0 from Eq. (10-5.17) and Eq. (10-3.27), where the constants C_n were given below this latter equation.

5. With η_0, the first component of the thermal conductivity is found from Eq. (10-5.19).

$$\lambda\,(1) = 1944\eta_0 \tag{10-5.19}$$

which is identical with the form of Eq. (10-3.28).

6. The second component for λ is calculated by

$$\lambda\,(2) = \left\{b_1 + b_2\left[b_3 - \ln\left(\frac{T_0}{b_4}\right)\right]^2\right\}\rho_0 \tag{10-5.20}$$

where T_0 and ρ_0 are given in Eqs. (10-5.17) and (10-5.18) and the coefficients b_n are:

$$b_1 = -2.5276\,E{-}4 \quad b_2 = 3.3433\,E{-}4 \quad b_3 = 1.12 \quad b_4 = 1.680\,E{+}2$$

7. The third component for λ is given as

$$\lambda (3) = \exp \left(a_1 + \frac{a_2}{T_0} \right) \left\{ \exp \left[\left(a_3 + \frac{a_4}{T_0^{3/2}} \right) \rho_0^{0.1} \right. \right.$$
$$\left. \left. + \left(\frac{\rho_0}{0.1617} - 1 \right) \rho_0^{1/2} \left(a_5 + \frac{a_6}{T_0} + \frac{a_7}{T_0^2} \right) \right] - 1.0 \right\} \times 10^{-3} \qquad (10\text{-}5.21)$$

Again ρ_0 and T_0 are from Eqs. (10-5.17) and (10-5.28) and the constants a_n are:

$$a_1 = -7.19771 \qquad a_2 = 85.67822 \qquad a_3 = 12.47183 \qquad a_4 = -984.6252$$
$$a_5 = 0.3594685 \qquad a_6 = 69.79841 \qquad a_7 = -872.8833$$

8. Finally, to determine λ^{**} in Eq. (10-5.10),

$$\lambda^{**} = [\lambda (1) + \lambda (2) + \lambda (3)]H \qquad (10\text{-}5.22)$$

$$H = \frac{(16.04 \times 10^{-3}/M')^{1/2} f^{1/2}}{h^{2/3}} \qquad (10\text{-}5.23)$$

For a low-pressure gas, λ (2) and λ (3) approach zero and the method reduces to the form given in Sec. 10-3.

For somewhat higher accuracy, Ely and Hanley suggest an additional correction factor in Eq. (10-5.22) which they call X. This parameter multiplies the right-hand side of Eq. (10-5.22).

$$X = \left\{ \left[1 - \frac{T}{f} \left(\frac{\partial f}{\partial T} \right)_v \right] \frac{0.288}{Z_c} \right\}^{3/2} \qquad (10\text{-}5.24)$$

With f from Eq. (10-5.15) and Θ from Eq. (10-5.13),

$$\left(\frac{\partial f}{\partial T} \right)_v = \frac{T_c}{190.4} \left(\frac{\partial \Theta}{\partial T} \right)_v \qquad (10\text{-}5.25)$$

$$\left(\frac{\partial \Theta}{\partial T} \right)_v = (\omega - 0.011) \left\{ -0.86276 \left(\frac{\partial \ln T^+}{\partial T} \right)_v \right.$$
$$\left. - (V^+ - 0.5) (0.46568) \left[\frac{\partial (1/T^+)}{\partial T} \right]_v \right\} \qquad (10\text{-}5.26)$$

If $T^+ = $ constant $= 2$, by Eq. (10-5.11), then $(\partial\Theta/\partial T)_v = 0$. If $T^+ = T_r = T/T_c$, then

$$\left(\frac{\partial \Theta}{\partial T} \right)_v = (\omega - 0.011) \left[\frac{-0.86276}{T} + (V^+ - 0.5) \frac{0.46568 T_c}{T^2} \right] \qquad (10\text{-}5.27)$$

With the value of $(\partial\Theta/\partial T)_v$ either as zero or from Eqs. (10-5.27) and (10-5.25), the correction factor X may be estimated. It is a number of the order of magnitude of unity.

Ely and Hanley tested their method on a large number of hydrocarbons up to densities where the materials were liquids and at temperatures from near the freezing point to above the critical temperature. They report a maximum error of 15 percent with more usual errors in the 3 to 8 percent range. The method does not allow for anomalies in the critical region, and its accuracy for nonhydrocarbons is in doubt. The procedure is illustrated in Example 10-4.

Example 10-4 Estimate the thermal conductivity of propylene at 473 K and 150 bar by using the methods of (a) Chung et al. and (b) Ely and Hanley. Under these conditions, Vargaftik [171] reports $\lambda = 6.64 \times 10^{-2}$ W/(m·K) and $V = 172.1$ cm³/mol. Also, the same author lists the low-pressure viscosity and thermal conductivity of propylene at 473 K as $\eta° = 134 \times 10^{-7}$ N·s/m² and $\lambda° = 3.89 \times 10^{-2}$ W/(m·K).

solution For both estimation techniques, we need certain parameters for propylene. From Appendix A:

$T_c = 364.9$ K

$P_c = 46.0$ bar

$V_c = 181$ cm³/mol

$Z_c = 0.274$

$\omega = 0.144$

$M = 42.081$ g/mol

$M' = 0.042081$ kg/mol

$\mu = 0.4$ debye

Also, since propylene is nonpolar, the association factor in Chung et al.'s method $\kappa = 0$.

The low-pressure heat capacity at constant pressure at 473 K is found from the equation and polynomial constants shown in Appendix A as 91.01 J/(mol·K). Thus

$$C_v = C_p - R = 91.01 - 8.31 = 82.70 \text{ J/(mol·K)}.$$

METHOD OF CHUNG ET AL. With the definition of Ψ given under Eq. (10-3.17), where

$$\alpha = \frac{C_v}{R} - \frac{3}{2} = \frac{82.70}{8.314} - \frac{3}{2} = 8.447$$

$$\beta = 0.7862 - 0.7109\omega + 1.3168\omega^2$$

$$= 0.7862 - (0.7109)(0.144) + (1.3168)(0.144)^2 = 0.7111$$

$$T_r = \frac{T}{T_c} = \frac{473}{364.9} = 1.296$$

$$Z = 2.0 + 10.5T_r^2 = 2.0 + (10.5)(1.296)^2 = 19.64$$

then

$$\Psi = 1 + 8.447 \frac{0.215 + (0.28288)\,(8.447) - (1.061)\,(0.7111) + (0.26665)\,(19.64)}{0.6366 + (0.7111)\,(19.64) + (1.061)\,(8.447)\,(0.7111)}$$

$$= 3.854$$

From Eq. (10-5.6)

$$y = \frac{\rho V_c}{6} = \frac{V_c}{6V} = \frac{181}{(6)\,(172.1)} = 0.1753$$

The values of B_i are found from Table 10-4, where $\omega = 0.144$ and $\kappa = 0$, and with Eq. (9-4.11),

$$\mu_r^4 = \left\{ \frac{(131.3)\,(0.4)}{[(181)\,(364.9)]^{1/2}} \right\}^4 = 1.74 \times 10^{-3}$$

As an example,

$$B_1 = 2.4166 + (7.4824 \times 10^{-1})\,(0.144) - (9.1858 \times 10^{-1})\,(1.74 \times 10^{-3}) = 2.5227$$

$$B_2 = -8.1358 \times 10^{-1} \qquad B_3 = 7.5328 \qquad B_4 = 1.3250 \times 10^1$$

$$B_5 = 9.0964 \times 10^{-1}$$

$$B_6 = -4.0034 \qquad B_7 = 1.0944 \times 10^2$$

With Eqs. (10-5.8) and (10-5.9),

$$G_1 = \frac{1 - (0.5)\,(0.1753)}{(1 - 0.1753)^3} = 1.627$$

For G_2,

$$\frac{B_1}{y}\,[1 - \exp\,(-B_4 y)] = \frac{2.5227}{0.1753}\,\{1 - \exp\,[-(13.250)\,(0.1753)]\} = 12.98$$

$$B_2 G_1 \exp\,(B_5 y) = (-0.81358)\,(1.627)\,\exp\,[(0.90964)\,(0.1753)] = -1.553$$

$$B_3 G_1 = (7.5328)\,(1.627) = 12.26$$

$$B_1 B_4 + B_2 + B_3 = (2.5227)\,(13.250) - 0.81358 + 7.5328 = 40.145$$

Thus

$$G_2 = \frac{(12.98 - 1.553 + 12.26)}{40.145} = 0.5900$$

and

$$q = \frac{3.586 \times 10^{-3}\,(T_c/M')^{1/2}}{V_c^{2/3}}$$

$$= \frac{3.586 \times 10^{-3}\,(364.9/0.042081)^{1/2}}{(181)^{2/3}} = 1.044 \times 10^{-2}$$

With Eq. (10-5.5),

$$\lambda = \frac{(31.2)\,(134 \times 10^{-7})\,(3.854)}{0.042081}\,[(0.5900)^{-1} - (4.0034)\,(0.1753)]$$

$$+ (1.044 \times 10^{-2})\,(109.44)\,(0.1753)^2\,(1.296)^{1/2}\,(0.5900)$$

$$= (3.829 \times 10^{-2})\,(0.9931) + 2.36 \times 10^{-2} = 6.16 \times 10^{-2}\ \text{W/(m·K)}$$

$$\text{Error} = \frac{6.16 - 6.64}{6.64} \times 100 = -7\%$$

Note that the first term in the final result (3.829×10^{-2}) would represent the estimated value of λ at low pressure. This result is in good agreement with the reported value of 3.89×10^{-2} W/(m·K) [171].

METHOD OF ELY AND HANLEY. Following the steps outlined in the text, with T_r = 473/364.9 = 1.296 and V_r = 172.1/181 = 0.951, then, from Eqs. (10-5.11) and (10-5.12), $T^+ = T_r = 1.296$, $V^+ = V_r = 0.951$. With Eqs. (10-5.13) and (10-5.14),

$$\theta = 1 + (0.144 - 0.011) \{0.09057 - 0.86276 \ln (1.296)$$

$$+ \left[0.31664 - \frac{0.46568}{1.296} \right] (0.951 - 0.5)\}$$

$$= 0.9797$$

$$\Phi = \{1 + (0.144 - 0.011) [0.39490 (0.951 - 1.02355)$$

$$- 0.93281 (0.951 - 0.75464) \ln (1.296)]\} \frac{0.288}{0.274}$$

$$= 1.040$$

Then, with Eqs. (10-5.15) through (10-5.18)

$$f = \frac{364.9}{190.4} (0.9797) = 1.876$$

$$h = \frac{181}{99.2} (1.040) = 1.898$$

$$T_0 = \frac{473}{1.876} = 252.1 \text{ K}$$

$$\rho_0 = \frac{16.04}{172.1} (1.898) = 0.1769$$

With Eq. (10-3.27) for $T_0 = 252.1$ K, $\eta_0 = 96.35 \times 10^{-7}$ N·s/m². By Eq. (10-5.19),

$$\lambda (1) = (1944) (96.35 \times 10^{-7}) = 1.873 \times 10^{-2}$$

Then, with Eq. (10-5.20)

$$\lambda (2) = \left\{ -2.5276 \times 10^{-4} + 3.3433 \times 10^{-4} \left[1.12 - \ln \left(\frac{252.1}{168.0} \right) \right]^2 \right\} (0.1769)$$

$$= 9.299 \times 10^{-5}$$

and, from Eq. (10-5.21)

$$\lambda (3) = \left[\exp \left(-7.19771 + \frac{85.67822}{252.1} \right) \right]$$

$$\times \left\{ \exp \left[\left(12.47183 - \frac{984.6252}{252.1^{3/2}} \right) (0.1769)^{0.1} \right. \right.$$

$$+ \left(\frac{0.1769}{0.1617} - 1 \right) (0.1769)^{1/2} \left(0.3594685 + \frac{69.79841}{252.1} \right.$$

$$- \left. \left. \frac{872.8833}{252.1^2} \right) \right] - 1.0 \right\} \times 10^{-3}$$

$$= 3.144 \times 10^{-2}$$

Then, with Eqs. (10-5.22) and (10-5.23),

$$H = \frac{(16.04 \times 10^{-3}/0.042081)^{1/2}(1.876)^{1/2}}{(1.898)^{2/3}} = 0.5516$$

$$\lambda^{**} = (1.873 \times 10^{-2} + 9.30 \times 10^{-5} + 3.144 \times 10^{-2}) (0.5516) = 2.77 \times 10^{-2} \text{ W/(m·K)}$$

To obtain the second term in Eq. (10-5.10), we follow the same procedure as shown under Eq. (10-3.20). $T_r = 473/364.9 = 1.296$, so $T^+ = T_r = 1.296$. With

Eqs. (10-3.22) and (10-3.23), $\Theta = 0.9738$ and $\Phi = 1.063$. [Note that these are somewhat different from the Θ and Φ values calculated from Eqs. (10-5.13) and (10-5.14) because no volume terms are included.] Then, with Eqs. (10-3.24) and (10-3.25), $f = 1.866$ and $h = 1.940$. Continuing, with Eqs. (10-3.26) and (10-3.27), $T_0 = 253.5$ K and $\eta_0 = 9.68 \times 10^{-6}$ N·s/m². With Eq. (10-3.31), $H = 0.542$ and, by Eq. (10-3.30), $\eta^* = 137 \times 10^{-7}$ N·s/m². Note that this term should represent the viscosity of pure propylene at low pressure and at 473 K; it is in agreement with the reported value of 134×10^{-7} N·s/m². Returning to Eq. (10-5.10),

$$\lambda = 2.77 \times 10^{-2} + \left(\frac{137 \times 10^{-7}}{0.042081}\right)(1.32)\,[82.70 - (3)(8.314)/2]$$

$$= 2.77 \times 10^{-2} + 3.02 \times 10^{-2} = 5.79 \times 10^{-2} \text{ W/(m·K)}$$

If the correction term Eq. (10-5.24) is used, by Eqs. (10-5.26) and (10-5.27),

$$\left(\frac{\partial\Theta}{\partial T}\right)_v = (0.144 - 0.011)\left[-\frac{0.86276}{473} + (0.951 - 0.5)\frac{(0.46568)(364.9)}{(473)^2}\right] = -1.97 \times 10^{-4}$$

$$\left(\frac{\partial f}{\partial T}\right)_v = \frac{364.9}{190.4} \times (-1.97 \times 10^{-4}) = -3.78 \times 10^{-4}$$

$$X = \left\{\left[1 + \left(\frac{473}{1.876}\right)(3.78 \times 10^{-4})\right]\frac{0.288}{0.274}\right\}^{3/2} = 1.235$$

The corrected value of λ is then

$$\lambda = (2.77 \times 10^{-2})(1.235) + 3.02 \times 10^{-2} = 6.44 \times 10^{-2} \text{ W/(m·K)}$$

$$\text{Error} = \frac{6.44 - 6.64}{6.64} \times 100 = -3\%$$

Discussion

Three methods for estimating the thermal conductivity of pure materials in the dense gas region were presented. All use the fluid density rather than pressure as a system variable. The low-density thermal conductivity is required in the Stiel and Thodos method [Eqs. (10.5.2) to (10.5.4)], but it is calculated as a part of the procedure in the Chung et al. [Eq. (10-5.5)]and Ely and Hanley [Eq. (10-5.10)] methods. None of the techniques are applicable for polar gases, and even for nonpolar materials, errors can be large. The Chung et al. and Ely and Hanley procedures are reported to be applicable over a wide density domain even into the liquid phase. No one of the methods appears to have a clear superiority over the others.

A number of alternative estimation methods were considered [26, 29, 34, 87, 112, 113, 124, 147, 165], but their accuracy or generality were significantly less than those of the three described. Riazi and Faghri [131] reduced the thermal conductivity by a term they refer to as the thermal conductivity at the critical point λ_c. They then relate $\lambda/\lambda_c = f(T_r, P_r, \omega)$. Unfortunately, values of λ_c are available for only a few materials, and it is not possible to estimate this parameter from low-pressure thermal conductivity data.

Zheng et al. [181] and Yorizane et al. [179] report high-pressure values

of λ for several simple gases and light hydrocarbons. Both found the Stiel and Thodos method to correlate their data reasonably well. Other recent papers showing new experimental data include Refs. 44, 127, and 165.

10-6 Thermal Conductivities of Low-Pressure Gas Mixtures

The thermal conductivity of a gas mixture is not usually a linear function of mole fraction. Generally, if the constituent molecules differ greatly in polarity, the mixture thermal conductivity is larger than would be predicted from a mole fraction average; for nonpolar molecules, the opposite trend is noted and is more pronounced the greater the difference in molecular weights or sizes of the constituents [48, 102]. Some of these trends are evident in Fig. 10-7, which shows experimental thermal conductivities for four systems. The argon-benzene system typifies a nonpolar case with different molecular sizes, and the methanol–n-hexane system is a case representing a significant difference in polarity. The linear systems benzene–n-hexane and ether-chloroform represent a balance between the effects of size and polarity.

Papers summarizing various methods for calculating mixture thermal conductivities can be found in Refs. 15, 83, 89, 110, 123, 158, 163, 164, 168. Many theoretical papers discussing the problems, approximations, and limitations of the various methods also have appeared. The theory for calculating the conductivity for *rare-gas* mixtures has been worked out in detail [13, 54, 92, 97, 98, 111]. The more difficult problem, however, is to modify monatomic mixture correlations to apply to polyatomic molecules. Many techniques have been proposed; all are essentially empirical, and most reduce to some form of the Wassiljewa equation. Corresponding states methods for low-pressure thermal conductivities have also been adapted for mixtures, but the results obtained in testing several were not encouraging.

Wassiljewa equation

In a form analogous to the theoretical relation for mixture viscosity, Eq. (9-5.13),

$$\lambda_m = \sum_{i=1}^{n} \frac{y_i \lambda_i}{\sum_{j=1}^{n} y_j A_{ij}} \tag{10-6.1}$$

where λ_m = thermal conductivity of the gas mixture
λ_i = thermal conductivity of pure i
y_i, y_j = = mole fraction of components i and j

A_{ij} = a function, as yet unspecified
A_{ii} = 1.0

This empirical relation was proposed by Wassiljewa in 1904 [178].

Mason and Saxena modification

Mason and Saxena [96] suggested that A_{ij} in Eq. (10-6.1) could be expressed as

$$A_{ij} = \frac{\epsilon[1 + (\lambda_{tri}/\lambda_{trj})^{1/2} (M_i/M_j)^{1/4}]^2}{[8(1 + M_i/M_j)]^{1/2}} \tag{10-6.2}$$

where M = molecular weight, g/mol
λ_{tr} = monatomic value of the thermal conductivity
ϵ = numerical constant near unity

Mason and Saxena proposed a value of 1.065 for ϵ, and Tondon and Saxena [162a] later suggested 0.85. As used here, $\epsilon = 1.0$.

From Eq. (10-2.3), noting for monatomic gases that $C_v = C_{tr} = \frac{3}{2}R$,

$$\frac{\lambda_{tri}}{\lambda_{trj}} = \frac{\eta_i}{\eta_j} \frac{M_j}{M_i} \tag{10-6.3}$$

Substituting Eq. (10-6.3) into Eq. (10-6.2) and comparing with Eq. (9-5.14) gives

$$A_{ij} = \phi_{ij} \tag{10-6.4}$$

where ϕ_{ij} is the interaction parameter for gas-mixture viscosity. Thus the relation for estimating mixture viscosities is also applicable to thermal conductivities by simply substituting λ for η. In this approximation, to determine λ_m, one needs data giving the pure component thermal conductivities and viscosities. An alternative way to proceed is to use Eqs. (10-6.1) and (10-6.2) but obtain the ratio of translational thermal conductivities from Eq. (10-3.14).

$$\frac{\lambda_{tri}}{\lambda_{trj}} = \frac{\Gamma_j [\exp(0.0464T_{ri}) - \exp(-0.2412T_{ri})]}{\Gamma_i [\exp(0.0464T_{rj}) - \exp(-0.2412T_{rj})]} \tag{10-6.5}$$

where Γ is defined by Eq. (10-3.12). With Eq. (10-6.5), values of A_{ij} become functions of the reduced temperatures of both i and j. However, with this latter approach, pure gas viscosities are not required. Both techniques are illustrated in Example 10-5.

Lindsay and Bromley [85] have also proposed a technique to estimate A_{ij}. It is slightly more complex than Eq. (10-6.2), and the results obtained do not differ significantly from the Mason-Saxena approach.

The Wassiljewa equation is capable of representing low-pressure mixture thermal conductivities with either a maximum or minimum as composition is varied. As Gray et al. [48] have shown, if $\lambda_1 < \lambda_2$,

$$\frac{\lambda_1}{\lambda_2} < A_{12}A_{21} < \frac{\lambda_2}{\lambda_1} \qquad \lambda_m \text{ varies monotonically with composition}$$

$$A_{12}A_{21} \geq \frac{\lambda_2}{\lambda_1} \qquad \lambda_m \text{ has a minimum value below } \lambda_1$$

$$\frac{\lambda_1}{\lambda_2} \geq A_{12}A_{21} \qquad \lambda_m \text{ has a maximum value above } \lambda_2$$

Corresponding states methods

Both the Chung et al. [27, 28] and Ely-Hanley [40] methods for estimating low-pressure thermal conductivities [Eqs. (10-3.17) and (10-3.20)] have been adapted to handle mixtures. The emphasis of these authors, however, was, to treat systems at high pressure and, if possible, as liquids. When their methods are used for low-pressure gas mixtures, the accuracy away from the pure components is often not particularly high. However, in their favor is the fact that pure component thermal conductivities are *not* required as input; the methods generate their own values of pure component conductivities.

To illustrate, consider the Chung et al. form. To use this procedure for mixtures, we need to have rules to obtain M', η, C_v, ω, and T_c for the mixture. η_m is found from Eq. (9-5.24), and in using this relation, one also obtains M_m, ω_m, and T_{cm} [Eqs. (9-5.28), (9-5.29), and (9-5.44)]; $M'_m = M_m/10^3$. For C_{vm}, a mole fraction average rule is used, i.e.,

$$C_{vm} = \sum_{i=1}^{n} y_i C_{vi} \qquad (10\text{-}6.6)$$

With these mixture values, the procedure to compute λ_m is identical with that used for the pure component conductivity (see Example 10-1). The method is also illustrated for a mixture in Example 10-5.

Discussion

Three techniques were suggested to estimate the thermal conductivity of a gas mixture at low pressure. Two employ the Wassiljewa formulation [Eq. (10-6.1)] and differ only in the manner $\lambda_{tri}/\lambda_{trj}$ is calculated. The third method (Chung et al.) uses a corresponding states approach. It is the least accurate, but it has the advantage that pure component thermal conductivities do not have to be known. The other two methods require either

experimental or estimated values of λ for all pure components. All three methods are illustrated in Example 10-5.

For nonpolar gas mixtures, we recommend the Wassiljewa equation with the Mason-Saxena relation for A_{ij}, where $\lambda_{\text{tr}i}/\lambda_{\text{tr}j}$ is calculated from Eq. (10-6.5). Errors will generally be less than 3 to 4 percent. For nonpolar-polar and polar-polar gas mixtures, none of the techniques examined were found to be particularly accurate. As an example, in Fig. 10-7, none predicted the maximum in λ_m for the methanol–n-hexane system. Thus, in such cases, errors greater than 5 to 8 percent may be expected when one employs the procedures recommended for nonpolar gas mixtures. For mixtures in which the sizes and polarities of the constituent molecules are not greatly different, λ_m can be estimated satisfactorily by a mole fraction average of the pure component conductivities (e.g., the benzene–n-hexane and ether-chloroform cases in Fig. 10-7).
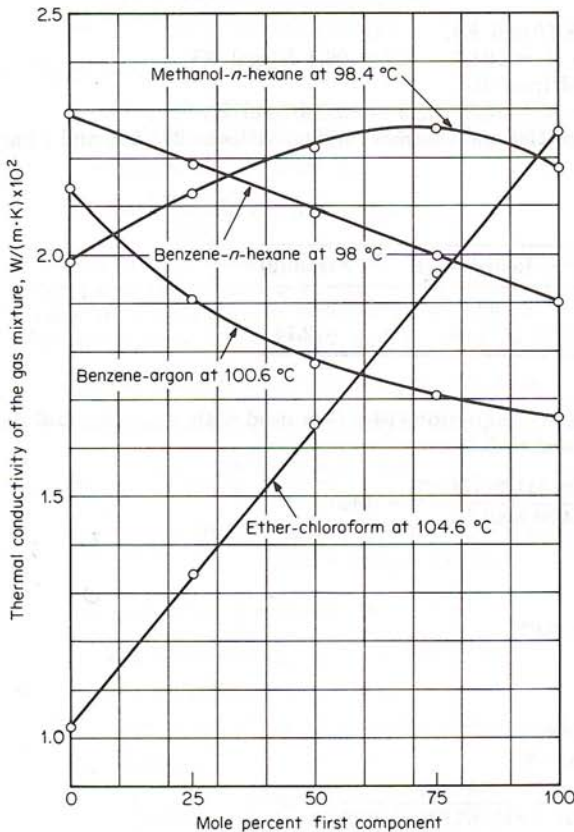
Figure 10-7 Typical gas-mixture thermal conductivities. *(From Ref. 10.)*

Example 10-5 Estimate the thermal conductivity of a gas mixture containing 25 mole percent benzene and 75 mole percent argon at 100.6°C and about 1 bar. The experimental value is 1.92×10^{-2} W/(m·K)[10].

From Appendix A, the following pure component constants are given:

	Benzene (1)	Argon (2)
T_c, K	562.2	150.8
P_c, bar	48.9	48.7
V_c, cm³/mol	259.	74.9
ω	0.212	0.001
Z_c	0.271	0.291
M, g/mol	78.114	39.948
M', kg/mol	0.078114	0.039948

Using the ideal-gas heat capacity constants for the two pure gases (Appendix A), at 373.8 K,

Benzene $C_p = 104.8$ J/(mol·K):
$C_v = C_p - R = 104.8 - 8.3 = 96.5$ J/(mol·K)

Argon $C_p = 20.8$ J/(mol·K)
$C_v = C_p - R = 20.8 - 8.3 = 12.5$ J/(mol·K)

The pure component viscosities and thermal conductivities at 373.8 K and 1 bar are:

	Benzene (1)	Argon (2)
η, N·s/m² × 10^7	92.5	271.
λ, W/(m·K) × 10^2	1.66	2.14

solution MASON AND SAXENA.   Equation (10-6.1) is used with $A_{12} = \phi_{12}$ and $A_{21} = \phi_{21}$ from Eqs. (9-5.14) and (9-5.15).

$$A_{12} = \frac{[1 + (92.5/271)^{1/2}(39.948/78.114)^{1/4}]^2}{\{[8[1 + (78.114/39.948)]\}^{1/2}} = 0.459$$

$$A_{21} = A_{12} \frac{\eta_2}{\eta_1} \frac{M_1}{M_2}$$

$$= 0.459 \frac{271}{92.5} \frac{78.114}{39.948} = 2.630$$

With Eq. (10-6.1)

$$\lambda_m = \frac{y_1 \lambda_1}{y_1 + y_2 A_{12}} + \frac{y_2 \lambda_2}{y_1 A_{21} + y_2}$$

$$= \left[\frac{(0.25)(1.66)}{0.25 + (0.75)(0.459)} + \frac{(0.75)(2.14)}{(0.25)(2.630) + 0.75} \right] \times 10^{-2}$$

$$= 1.84 \times 10^{-2} \text{ W/(m·K)}$$

$$\text{Error} = \frac{1.84 - 1.92}{1.92} \times 100 = -4.2\%$$

MASON AND SAXENA FORM WITH EQ. (10-6.5). In this case, $\lambda_{tr1}/\lambda_{tr2}$ is obtained from Eq. (10-6.5). Γ is determined with Eq. (10-3.12).

$$\Gamma_1 = 210 \left[\frac{(562.2) \times (78.114)^3}{(48.9)^4} \right]^{1/6} = 398.7$$

$$\Gamma_2 = 210 \left[\frac{(150.8) \times (39.948)^3}{(48.7)^4} \right]^{1/6} = 229.6$$

At 373.8 K, $T_{r_1} = 373.8/562.2 = 0.665$; $T_{r_2} = 373.8/150.8 = 2.479$. Then,

$$\frac{\lambda_{tr1}}{\lambda_{tr2}} = \frac{229.6\{\exp\left[(0.0464)(0.665)\right] - \exp\left(-0.2412)(0.665)\right]\}}{398.7\{\exp\left[(0.0464)(2.479)\right] - \exp\left[(-0.2412)(2.479)\right]\}}$$

$$= 0.1808$$

$$\frac{\lambda_{tr2}}{\lambda_{tr1}} = (0.1808)^{-1} = 5.536$$

Inserting these values into Eq. (10-6.2) with $\epsilon = 1.0$ gives

$$A_{12} = \frac{[1 + (0.1808)^{1/2}(78.114/39.948)^{1/4}]^2}{\{8[1+(78.114/39.948)]\}^{1/2}} = 0.4645$$

$$A_{21} = \frac{[1 + (5.536)^{1/2}(39.948/78.114)^{1/4}]^2}{\{8[1 + (39.948/78.114)]\}^{1/2}} = 2.571$$

Then, using Eq. (10-6.1),

$$\lambda_m = \left[\frac{(0.25)(1.66)}{0.25 + (0.75)(0.4645)} + \frac{(0.75)(2.14)}{(0.25)(2.571)+0.75} \right] \times 10^{-2}$$

$$= 1.85 \times 10^{-2} \quad \text{W/(m·K)}$$

$$\text{Error} = \frac{1.85-1.92}{1.92} \times 100 = -3.6\%$$

CHUNG ET AL. With this method, we use the relations described in Chap. 9 to determine the mixture properties η_m, M'_m, ω_m, and T_{cm}. (See Example 9-8.) In this case, at 25 mole percent benzene, $\eta_m = 182.2 \ \mu P = 182.2 \times 10^{-7} \ \text{N·s/m}^2$, $M'_m = 0.04631$ kg/mol, $\omega_m = 0.0817$, and $T_{cm} = 277.4$ K. From Eq. (10-6.6),

$$C_{vm} = (0.25)(96.5) + (0.75)(12.5) = 33.5 \ \text{J/(mol·K)}$$

The mixture thermal conductivity is then found from Eq. (10-3.17).

$$\lambda_m = \frac{(\eta_m C_{vm}/M'_m)(3.75\Psi_m)}{C_{vm}/R} = \frac{\eta_m R}{M'_m} (3.75\Psi_m)$$

$$\Psi_m = 1 + \frac{\alpha_m[0.215 + 0.28288\alpha_m - 1.061\beta_m + 0.26665Z_m]}{0.6366 + \beta_m Z_m + 1.061\alpha_m\beta_m}$$

$$\alpha_m = (C_{vm}/R) - \frac{3}{2} = (33.5/8.31) - \frac{3}{2} = 2.53$$

$$\beta_m = 0.7862 - 0.7109\omega_m + 1.3168\omega_m^2 = 0.7369$$

$$T_{rm} = 373.8/277.4 = 1.348$$

$$Z_m = 2.0 + 10.5 \ T_{rm}^2 = 2.0 + (10.5)(1.348)^2 = 21.07$$

$$\Psi_m = 1.812$$

$$\lambda_m = \left[(182.2 \times 10^{-7}) \frac{8.314)}{0.04631} \right] [(3.75)(1.812)]$$

$$= 2.22 \times 10^{-2} \ \text{W/(m·K)}$$

$$\text{Error} = \frac{2.22 - 1.92}{1.92} \times 100 = 16\%$$

10-7   Thermal Conductivities of Gas Mixtures at High Pressures

There are few experimental data for gas mixtures at high pressures and, even here, most studies are limited to simple gases and light hydrocarbons. The nitrogen–carbon dioxide system was studied by Keyes [72], and Comings and his colleagues reported on ethylene mixtures with nitrogen and carbon dioxide [66], rare gases [126], and binaries containing carbon dioxide, nitrogen, and ethane [47]. Rosenbaum and Thodos investigated methane-carbon dioxide [139] and methane–carbon tetrafluoride [138] binaries. Binaries containing methane, ethane, nitrogen, and carbon dioxide were also reported by Christensen and Fredenslund [25], and data for systems containing nitrogen, oxygen, argon, methane, ethylene, and carbon dioxide were published by Zheng et al. [181] and Yorizane et al. [180].

Recent theoretical papers [26, 71, 93, 112, 113] have not, as yet, led to accurate predictive techniques.

We present below three estimation methods. All are modifications of procedures developed earlier for low- and high-pressure pure gas thermal conductivities.

Stiel and Thodos modification

Equations (10-5.2) to (10-5.4) were suggested as a way to estimate the high-pressure thermal conductivity of a pure gas. This procedure may be adapted for mixtures if mixing and combining rules are available to determine T_{cm}, P_{cm}, V_{cm}, Z_{cm} and M_m. Yorizane et al. [180] have studied this approach and recommend the following:

$$T_{cm} = \frac{\sum_i \sum_j y_i y_j V_{cij} T_{cij}}{V_{cm}} \tag{10-7.1}$$

$$V_{cm} = \sum_i \sum_j y_i y_j V_{cij} \tag{10-7.2}$$

$$\omega_m = \sum_i y_i \omega_i \tag{10-7.3}$$

$$Z_{cm} = 0.291 - 0.08 \omega_m \tag{10-7.4}$$

$$P_{cm} = Z_{cm} R T_{cm} / V_{cm} \tag{10-7.5}$$

$$M_m = \sum_i y_i M_i \tag{10-7.6}$$

$$T_{cii} = T_{ci} \tag{10-7.7}$$

$$T_{cij} = (T_{ci} T_{cj})^{1/2} \tag{10-7.8}$$

$$V_{cii} = V_{ci} \tag{10-7.9}$$

$$V_{cij} = \tfrac{1}{8} [(V_{ci})^{1/3} + (V_{cj})^{1/3}]^3 \tag{10-7.10}$$

Using these simple rules, they found they could correlate their high-pressure thermal conductivity data for CO_2-CH_4 and CO_2-Ar systems quite well. In Fig. 10-8 we show a plot of λ_m for the CO_2-Ar system at 298 K. This case is interesting because the temperature is slightly below the critical temperature of CO_2 and, at high pressure, λ for carbon dioxide increases more rapidly than that for argon. The net result is that the λ_m composition curves are quite nonlinear. Still, the Stiel-Thodos method, with Eqs. (10-7.1) through (10-7.10), appears to give a quite satisfactory fit to the data. We illustrate the approach in Example 10-6.

Example 10-6 Estimate the thermal conductivity of a methane (1)–carbon dioxide (2) mixture containing 75.5 mole percent methane at 370.8 K and 174.8 bar. Rosenbaum and Thodos [139] show an experimental value of 5.08×10^{-2} W/$(m \cdot K)$; these same investigators report that, for the mixture, $V = 159$ cm^3/mol and, at 1 bar, $\lambda_m^\circ = 3.77 \times 10^{-2}$ W/$(m \cdot K)$.
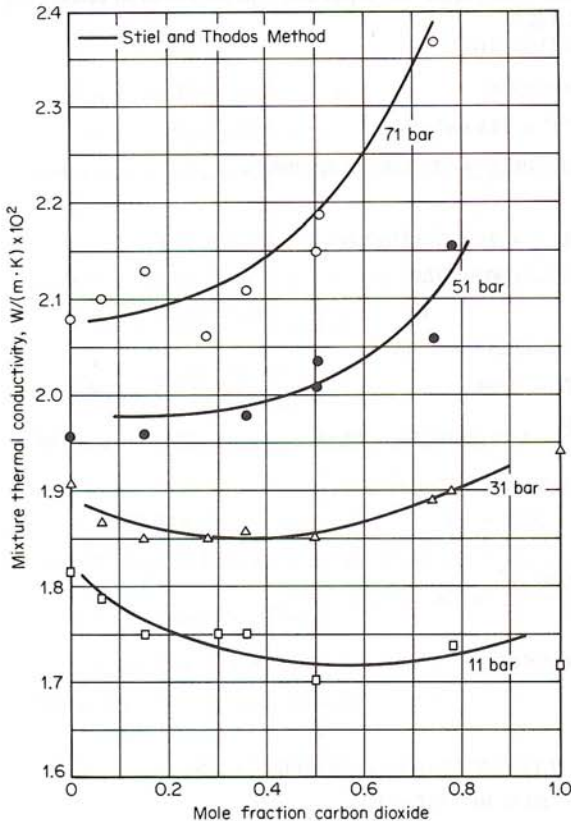
Figure 10-8 High-pressure thermal conductivities of the argon–carbon dioxide system. (*Experimental Data from Ref. 180.*)

solution From Appendix A, we list pure component constants for methane and carbon dioxide that will be used in this example and in Examples 10-7 and 10-8.

	CH$_4$ (1)	CO$_2$ (2)
T_c, K	190.4	304.1
P_c, bar	46.0	73.8
V_c, cm^3/mol	99.2	93.9
Z_c	0.288	0.274
ω	0.011	0.239
μ, debye	0	0
C_p J/(mol·K)	39.65	40.20
C_v, J/(mol·K)	31.33	31.89
M, g/mol	16.043	44.010
M', kg/mol	0.01604	0.04401

The heat capacities were calculated from the equation and polynomial constants in Appendix A at $T = 370.8$ K.
With Eqs. (10-7.1) through (10-7.10),

$$T_{c12} = [(190.4)(304.1)]^{1/2} = 240.6 \text{ K}$$

$$V_{c12} = \tfrac{1}{8}[(99.2)^{1/3} + (93.9)^{1/3}]^3 = 96.5 \text{ cm}^3/\text{mol}$$

$$V_{cm} = (0.755)^2(99.2) + (0.245)^2(93.8) + (2)(0.755)(0.245)(96.5)$$

$$= 97.9 \text{ cm}^3/\text{mol}$$

$$T_{cm} = [(0.755)^2(190.4)\,(99.2) + (0.245)^2(304.1)(93.9)$$
$$+ (2)(0.755)(0.245)(240.6)(96.5)]/97.9$$

$$= 215.2 \text{ K}$$

$$\omega_m = (0.755)(0.011) + (0.245)(0.239) = 0.067$$

$$Z_{cm} = 0.291 - (0.08)(0.067) = 0.286$$

$$P_{cm} = \frac{(0.286)(8.314)(215.2)}{97.9 \times 10^{-6}} = 5.24 \times 10^6 \text{ Pa} = 52.4 \text{ bar}$$

$$M_m = (0.755)(16.04) + (0.245)(44.01) = 22.9 \text{ g/mol}$$

With Eq. (10-3.12),

$$\Gamma = (210) \left[\frac{(215.2)(22.9)^3}{(52.4)^4} \right]^{1/6} = 176$$

and

$$\rho_{rm} = \frac{V_{cm}}{V_m} = \frac{97.9}{159} = 0.616$$

Using Eq. (10-5.3),

$$(\lambda_m - \lambda_m^\circ)\,[(176)(0.286)^5] = (1.14 \times 10^{-2})\{\exp\,[(0.67)(0.616)] - 1.069\}$$

$$\lambda_m - \lambda_m^\circ = 1.50 \times 10^{-2} \text{ W/(m·K)}$$

$$\lambda_m = (1.50 + 3.77)(10^{-2}) = 5.27 \times 10^{-2} \text{ W/(m·K)}$$

$$\text{Error} = \frac{5.27 - 5.08}{5.08} \times 100 = 4\%$$

Chung et al. method [27, 28]

To apply this method to estimate the thermal conductivities of high-pressure gas mixtures, one must combine the high-pressure *pure* component relations with the mixing rules given in Secs. 10-6 and in 9-5. To be specific, Eq. (10-5.5) is employed with all variables subscripted with m to denote them as mixture properties. Example 10-7 illustrates the procedure in detail.

Example 10-7 Repeat Example 10-6 by using the Chung et al. approach.

solution For the methane (1)–carbon dioxide (2) system, the required pure component properties were given in Example 10-6.
To use Eq. (10-5.5), let us first estimate η_m° with the procedures in Chap. 9. From Eqs. (9-4.6) and (9-4.7),

$$\left(\frac{\epsilon}{k}\right)_1 = \frac{190.4}{1.2593} = 151.2 \text{ K}$$

$$\left(\frac{\epsilon}{k}\right)_2 = \frac{304.1}{1.2593} = 241.5 \text{ K}$$

$$\sigma_1 = (0.809)(99.2)^{1/3} = 3.745 \text{ Å}$$

$$\sigma_2 = (0.809)(93.9)^{1/3} = 3.677 \text{ Å}$$

Interaction values are then found from Eqs. (9-5.32), (9-5.35), (9-5.37), and (9-5.40).

$$\sigma_{12} = [(3.745)(3.677)]^{1/2} = 3.711 \text{ Å}$$

$$(\epsilon/k)_{12} = [(151.2)(241.5)]^{1/2} = 191.1 \text{ K}$$

$$\omega_{12} = \frac{(0.011+0.239)}{2} = 0.125$$

$$M_{12} = \frac{(2)(16.04)(44.01)}{(16.04 + 44.01)} = 23.51$$

With $y_1 = 0.755$ and $y_2 = 0.245$, using Eqs. (9-5.25) to (9-5.29) and Eq. (9-5.41),

$$\sigma_m = 3.728 \text{ Å} \qquad (\epsilon/k)_m = 171.0 \text{ K} \qquad T^* = 2.168$$

$$M_m = 20.89 \text{ g/mol} \qquad \omega_m = 0.066 \qquad F_m = 0.982$$

so, with Eq. (9-4.3), $\Omega_v = 1.144$. Then, with Eq. (9-5.24),

$$\eta_m^\circ = (26.69)(0.982) \frac{[(20.89)(370.8)]^{1/2}}{(3.728)^2(1.144)}$$

$$= 145.1 \ \mu\text{P} = 145.1 \times 10^{-7} \text{ N·s/m}^2$$

With Eqs. (9-5.43) and (9-5.44),

$$V_{cm} = \left(\frac{\sigma_m}{0.809}\right)^3 = 97.85 \text{ cm}^3/\text{mol}$$

$$T_{cm} = (1.2593)\left(\frac{\epsilon}{k}\right)_m = 215.3 \text{ K}$$

$$T_r = \frac{T}{T_{cm}} = \frac{370.8}{215.3} = 1.722$$

C_v for the mixture is found with Eq. (10-6.6) as 31.47 J/(mol·K), and Ψ is determined as indicated under Eq. (10-3.17) with

$$\alpha_m = \frac{31.47}{8.314} - \frac{3}{2} = 2.285$$

$$\beta_m = 0.7862 - (0.7109)(0.066) + (1.3168)(0.066)^2 = 0.745$$

$$Z = 2.0 + (10.5)(1.722)^2 = 33.14$$

$$\Psi = 1.750$$

and $\qquad M' = M/10^3 = 20.89 \times 10^{-3}$ kg/mol

With Eqs. (10-5.6) to (10-5.8) and Table 10-4,

$$y_m = 0.1026$$

$$G_1 = 1.313$$

$$G_2 = 0.6522$$

$B_1 = 2.466, B_2 = -0.6089, B_3 = 6.982, B_4 = 13.95,$

$B_5 = 0.8469, B_6 = -5.019,$ and $B_7 = 99.54$

$$q = \frac{(3.586 \times 10^{-3})(215.3/20.89 \times 10^{-3})^{1/2}}{(97.85)^{2/3}} = 1.714 \times 10^{-2}$$

Finally, substituting these values into Eq. (10-5.5),

$$\lambda_m = \frac{(31.2)(145.1 \times 10^{-7})(1.750)}{20.89 \times 10^{-3}} [(0.6522)^{-1} - (5.019)(0.1026)]$$

$$+ (1.714 \times 10^{-2})(99.54)(0.1026)^2(1.722)^{1/2}(0.6522)$$

$$= 5.40 \times 10^{-2} \text{ W/(m·K)}$$

$$\text{Error} = \frac{5.40 - 5.08}{5.08} \times 100 = 6\%$$

If the pressure were reduced to 1 bar, y_m would become quite small and G_2 would be essentially unity. In that case, $\lambda_m^{\circ} = 3.79 \times 10^{-2}$ W/(m·K), a value very close to the value reported experimentally (3.77×10^{-2} W/(m·K)).

Whereas the procedure appears tedious, it is readily programmed for computer use. The error found in Example 10-7 is typical for this method when simple gas mixtures are treated. As noted before, the Chung et al. method should not be used for polar gases. Its accuracy for nonpolar gas mixtures containing other than simple gases or light hydrocarbons is in doubt.

Method of Ely and Hanley [40, 51]

For gas mixtures at high pressure, the thermal conductivity is determined by a combination of the techniques introduced for low-pressure gases (Sec. 10-3) and high-pressure gases (Sec. 10-5) with appropriate mixing rules. The thermal conductivity of the mixture is given by:

$$\lambda_m = \lambda^{**}_m + \lambda'_m \qquad (10\text{-}7.11)$$

where
$$\lambda'_m = \sum_i \sum_j y_i y_j \lambda'_{ij} \qquad (10\text{-}7.12)$$

$$\lambda'_{ii} = \lambda'_i \qquad (10\text{-}7.13)$$

$$\lambda'_{ij} = \frac{2\lambda'_i \lambda'_j}{\lambda'_i + \lambda'_j} \qquad (10\text{-}7.14)$$

$$\lambda'_i = (\eta_i^*/M'_i)(1.32)\left(C_{v_i} - \frac{3R}{2}\right) \qquad (10\text{-}7.15)$$

The definition of λ'_i is identical with the second term on the right-hand side of Eq. (10-3.20). The procedure described under this equation should be followed to obtain numerical values. λ'_i is a function of T_c, C_v, and M' of each component as well as the system temperature T.

The term λ^{**}_m is determined in the same manner as λ^{**} in Eq. (10-5.10), although appropriate mixing rules must be specified to account for variations in composition. Procedural steps 1, 2, and 3 [under Eq. (10-5.10)] are followed for each component in the mixture to obtain f_i and h_i. We then obtain h_m, f_m, and M'_m from the following mixing and combining rules:

$$h_m = \sum_i \sum_j y_i y_j h_{ij} \qquad (10\text{-}7.16)$$

$$h_{ii} = h_i \qquad (10\text{-}7.17)$$

$$h_{ij} = \tfrac{1}{8}\left[(h_i)^{1/3} + (h_j)^{1/3}\right]^3 \qquad (10\text{-}7.18)$$

$$f_m = \frac{\sum_i \sum_j y_i y_j f_{ij} h_{ij}}{h_m} \qquad (10\text{-}7.19)$$

$$f_{ii} = f_i \qquad (10\text{-}7.20)$$

$$f_{ij} = (f_i f_j)^{1/2} \qquad (10\text{-}7.21)$$

$$M'_m = \left[\sum_i \sum_j y_i y_j M_{ij}^{-1/2} f_{ij}^{1/2} h_{ij}^{-4/3}\right]^{-2} (f_m h_m^{-8/3}) \qquad (10\text{-}7.22)$$

$$M'_{ii} = M'_i \qquad (10\text{-}7.23)$$

$$M'_{ij} = \frac{2M'_i M'_j}{M'_i + M'_j} \qquad (10\text{-}7.24)$$

T_0 and ρ_0 are found from

$$T_0 = \frac{T}{f_m} \qquad (10\text{-}7.25)$$

$$\rho_0 = \frac{16.04}{V_m} h_m \qquad (10\text{-}7.26)$$

with T the system temperature, in kelvins, and V_m the molar volume of the mixture, cm³/mol. λ_m (1), λ_m (2), and λ_m (3) are then calculated from

Eqs. (10-5.19) to (10-5.21) with the T_0, ρ_0 values obtained above. Then,

$$H_m = \left(\frac{16.04 \times 10^{-3}}{M'_m}\right)^{1/2} \frac{f_m^{1/2}}{h_m^{2/3}} \tag{10-7.27}$$

$$\lambda^{**}_m = [\lambda_m(1) + \lambda_m(2) + \lambda_m(3)]H_m \tag{10-7.28}$$

If desired, the correction term X, defined in Eq. (10-5.24), may be used to multiply the right-hand side of Eq. (10-7.28). The mixture thermal conductivity is then found from Eq. (10-7.11).

Ely and Hanley tested their method on a number of binary hydrocarbon mixtures over a wide range of densities. They report an average absolute error of about 7 percent, although, in some cases, significantly larger deviations were found. The technique is illustrated in Example 10-8.

Example 10-8 Repeat Example 10-6 by using the Ely-Hanley procedure.

solution The pure component properties for both components of the methane (1), carbon dioxide (2) binary are given at the beginning of the solution of Example 10-6.

We will use Eq. (10-7.11). First λ^{**}_m is estimated. $T_c(1) = 190.4$ K, $T_c(2) = 304.1$ K, $V_c(1) = 99.2$ cm^3/mol, $V_c(2) = 93.9$ cm^3/mol, $T = 370.8$ K, and $V_m = 159.0$ cm^3/mol. Then, $T_r(1) = 370.8/190.4 = 1.947$; $T_r(2) = 370.8/304.1 = 1.219$, $V_r(1) = 159.0/99.2 = 1.603$, and $V_r(2) = 159.0/93.9 = 1.693$. With Eqs. (10-5.11) and (10-5.12),

$$T^+(1) = T_r(1) = 1.947 \qquad T^+(2) = T_r(2) = 1.219$$
$$V^+(1) = V_r(1) = 1.603 \qquad V^+(2) = V_r(2) = 1.693$$

Then, with Eqs. (10-5.13) to (10-5.16).†

$$\Theta(1) = 1.0 \qquad \Theta(2) = 0.964$$
$$\phi(1) = 1.0 \qquad \phi(2) = 1.073$$
$$f(1) = 1.0 \qquad f(2) = 1.540$$
$$h(1) = 1.0 \qquad h(2) = 1.016$$

Now, with Eqs. (10-7.16) through (10-7.24) with $y(1) = 0.755$, $y(2) = 0.245$,

$$h(1\text{-}2) = \tfrac{1}{8}[(1.0)^{1/3} + (1.016)^{1/3}]^3 = 1.008$$
$$h_m = (0.755)^2(1.0) + (0.245)^2(1.016) + (2)(0.755)(0.245)(1.008)$$
$$= 1.004$$
$$f(1\text{-}2) = [(1.0)(1.540)]^{1/2} = 1.241$$
$$f_m = (0.755)^2(1.0) + (0.245)^2(1.540) + (2)(0.755)(0.245)(1.241)$$
$$= 1.122$$

---

†Note that, since methane is the *reference* fluid, all relative terms, Θ, ϕ, f, and h, become unity.

$$M' \ (1\text{-}2) = \frac{(2)(0.01604)(0.04401)}{(0.01604 + 0.04401)} = 0.02351$$

$$M'_m = [(0.755)^2(0.01604)^{-1/2}(1.0)^{1/2}(1.0)^{-4/3} + (0.245)^2(0.04401)^{-1/2}(1.540)^{1/2}(1.016)^{-4/3} +$$
$$(2)(0.755)(0.245)(0.02351)^{-1/2}(1.241)^{1/2}(1.008)^{-4/3}] \times [(1.122)(1.004)^{-8/3}]$$
$$= 0.01969$$

Thus, with Eqs. (10-7.25) and (10-7.26),

$$T_0 = \frac{370.8}{1.122} = 330.5 \ K$$

$$\rho_0 = \left(\frac{16.04}{159}\right)(1.004) = 0.1013 \ g/cm^3$$

With Eq. (10-3.27), $\eta_0 = 1.225 \times 10^{-5} \ N \cdot s/m^2$ and, by Eq. (10-5.19),

$$\lambda_m \ (1) = (1944)(1.225 \times 10^{-5}) = 2.38 \times 10^{-2} \ W/(m \cdot K)$$

and, by Eqs. (10-5.20) and (10-5.21),

$$\lambda_m \ (2) = -1.89 \times 10^{-5} \simeq 0$$

$$\lambda_m \ (3) = 1.618 \times 10^{-2} \ W/(m \cdot K)$$

Then by Eqs. (10-7.27) and (10-7.28),

$$H_m = \frac{(0.01604/0.01969)^{1/2}(1.122)^{1/2}}{(1.004)^{2/3}} = 0.953$$

$$\lambda_m^{**} = (2.38 + \sim 0 + 1.62)(10^{-2})(0.953) = 3.81 \times 10^{-2} \ W/(m \cdot K)$$

Next, we need to estimate λ' (1) and λ' (2) as given by Eq. (10-7.15) and calculated as shown under Eq. (10-3.20). We show the steps and results below.

Parameter	Equation	CH_4 (1)	CO_2 (2)
T_r	—	1.947	1.219
T^+	(10-3.21)	1.947	1.219
θ	(10-3.22)	1.0	0.959
ϕ	(10-3.23)	1.0	1.088
f	(10-3.24)	1.0	1.532
h	(10-3.25)	1.0	1.030
T_0, K	(10-3.26)	370.8	242.0
η_0, N·s/m^2	(10-3.27)	1.348×10^{-5}	9.279×10^{-6}
H	(10-3.31)	1.0	0.7326
η^*, N·s/m^2	(10-3.30)	1.345×10^{-5}	1.865×10^{-5}
C_v, J/(mol·K)	—	31.33	31.89
M', kg/mol	—	0.01604	0.04401
λ', W/(m·K)	(10-7.15)	2.087×10^{-2}	1.086×10^{-2}

With Eq. (10-7.14),

$$\lambda' \ (1\text{-}2) = \frac{(2)(2.087 \times 10^{-2})(1.086 \times 10^{-2})}{(2.087 \times 10^{-2} + 1.086 \times 10^{-2})}$$

$$= 1.429 \times 10^{-2} \ W/(m \cdot K)$$

and, by Eq. (10-7.12),

$$\lambda'_m = (0.755)^2(2.087 \times 10^{-2}) + (0.245)^2(1.086 \times 10^2)$$
$$+ (2)(0.755)(0.245)(1.429 \times 10^{-2})$$
$$= 1.78 \times 10^{-2} \text{ W/(m·K)}$$

So, with Eq. (10-7.11),

$$\lambda_m = 3.81 \times 10^{-2} + 1.78 \times 10^{-2} = 5.59 \times 10^{-2} \text{ W/(m·K)}$$

$$\text{Error} = \frac{5.59 - 5.08}{5.08} \times 100 = 10\%$$

No correction [i.e., Eq. (10-5.24)] was used in this example.

Discussion

Of the three methods presented to estimate the thermal conductivity of high-pressure (or high-density) gas mixtures, all have been tested on available data and shown to be reasonably reliable with errors averaging about 5 to 7 percent. However, the database used for testing is small and comprises, primarily, permanent gases and light hydrocarbons. None are believed applicable to polar fluid mixtures. Chung et al. and Ely and Hanley have also tested their methods on more complex (hydrocarbon) systems at densities which are in the liquid range with quite encouraging results.

It is interesting to note that none of the methods are interpolative in nature, i.e., the pure component conductivities at the system pressure and temperature are not required. Yorizane et al. [180] did investigate the use of the Wassiljewa equation (10-6.1) to account for composition variations while using high-pressure thermal conductivities as "hinge" values. They report that this technique was not particularly accurate.

For simple hand calculation of one or a few values of λ_m, the Stiel and Thodos method is certainly the simplest. If many values are to be determined, the somewhat more complex, but probably more accurate, methods of Chung et al. or Ely and Hanley should be programmed and used.

10-8   Thermal Conductivities of Liquids

For many simple organic liquids, the thermal conductivities are between 10 and 100 times larger than those of the low-pressure gases at the same temperature. There is little effect of pressure, and raising the temperature usually decreases the thermal conductivities. These characteristics are similar to those noted for liquid viscosities, although the temperature dependence of the latter is pronounced and nearly exponential, whereas that for thermal conductivities is weak and nearly linear.

Values of λ_L for most common organic liquids range between 0.10 and 0.17 W/(m·K) at temperatures below the normal boiling point, but water,

ammonia, and other highly polar molecules have values several times as large. Also, in many cases the dimensionless ratio $M\lambda/R\eta$ is nearly constant (for nonpolar liquids) between values of 2 and 3, so that viscous liquids have a correspondingly larger thermal conductivity. Liquid metals and some organosilicon compounds have large values of λ_L; the former often are 100 times larger than those for normal organic liquids. The solid thermal conductivity at the melting point is approximately 20 to 40 percent larger than that of the liquid. Liquid thermal conductivity data have been compiled and evaluated by Jamieson et al. [64]. In Table 10-5, we show the thermal conductivities of some liquids as a function of temperature [64].

The difference between transport property values in the gas phase and the values in the liquid phase indicates a distinct change in mechanism of energy (or momentum or mass) transfer, i.e.,

$$\frac{\lambda_L}{\lambda_G} \simeq 10 \text{ to } 100 \qquad \frac{\eta_L}{\eta_G} \simeq 10 \text{ to } 100 \qquad \frac{D_L}{D_G} \simeq 10^{-4}$$

In the gas phase, the molecules are relatively free to move about and transfer momentum and energy by a collisional mechanism. The intermolecular force fields, though not insignificant, do not drastically affect the value of λ, η, or D. That is, the intermolecular forces are reflected solely in the collision integral terms Ω_v and Ω_D, which are really ratios of collision integrals for a real force field and an artificial case in which the molecules are rigid, noninteracting spheres. The variation of Ω_v or Ω_D from unity then yields a rough quantitative measure of the importance of intermolecular forces in affecting gas phase transport coefficients. Reference to Eq. (9-4.3) (for Ω_v) or Eq. (11-3.6) (for Ω_D) shows that Ω values are often near unity. One then concludes that a rigid, noninteracting spherical molecular model yields a low-pressure transport coefficient λ,† η, or D not greatly different from that computed when intermolecular forces are included.

In the liquid, however, this hypothesis is not even roughly true. The close proximity of molecules to one another emphasizes strongly the intermolecular forces of attraction. There is little wandering of the individual molecules, as evidenced by the low value of liquid diffusion coefficients, and often a liquid is modeled as a lattice with each molecule caged by its nearest neighbors. Energy and momentum are primarily exchanged by oscillations of molecules in the shared force fields surrounding each molecule. McLaughlin [88] discusses in more detail the differences in transport mechanisms between a dense gas or liquid and a low-pressure gas.

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†λ in this case is the monatomic value, *not* including contributions from internal energy transfer mechanisms.

TABLE 10-5 Thermal Conductivities of Some Liquids[1]

$\lambda = A + BT + CT^2$, λ in W/(m·K) and T in kelvins

Formula	Name	A	B	C	λ	T	Range
He	helium	-3.995E-1	6.490E-1	-2.094E-1	8.33E-2	1.9	1.9 to 2.2
		4.118E-2	-1.833E-2	3.789E-3	2.11E-2	3.2	2.2 to 4.9
Ne	neon	1.374E-2	8.392E-3	-1.726E-4	1.01E-1	34	25 to 43
A	argon	1.862E-1	-4.121E-4	-3.589E-6	1.09E-1	100	84 to 145
H2	hydrogen	-8.546E-3	1.036E-2	-2.239E-4	1.11E-1	23	14 to 32
N2	nitrogen	2.629E-1	-1.545E-3	-9.450E-7	1.15E-1	91	64 to 121
O2	oxygen	2.444E-1	-8.813E-4	-2.023E-6	1.49E-1	90	55 to 138
F2	fluorine	2.565E-1	-6.795E-4	-4.958E-6	1.34E-1	103	54 to 133
Cl2	chlorine	2.508E-1	-2.022E-4	-6.381E-7	1.37E-1	293	172 to 405
Br2	bromine	1.608E-1	-1.285E-5	-3.366E-7	1.28E-1	293	266 to 573
I2	iodine	1.340E-1	4.296E-5	-2.031E-7	1.15E-1	429	386 to 785
HF	hydrogen fluoride	7.100E-1	-8.622E-4	-6.440E-7	4.02E-1	293	190 to 438
HCl	hydrogen chloride	4.487E-1	-7.721E-5	-2.756E-6	1.89E-1	293	159 to 304
HBr	hydrogen bromide	2.428E-1	1.605E-4	-1.721E-6	1.42E-1	293	186 to 343
HI	hydrogen iodide	2.599E-1	-4.300E-5	-9.098E-7	1.69E-1	293	223 to 383
CO	carbon monoxide	1.991E-1	1.386E-5	-8.971E-6	1.52E-1	73	68 to 128
CO2	carbon dioxide	4.070E-1	-8.438E-4	-9.626E-7	7.69E-2	293	217 to 299
SO2	sulfur dioxide	8.964E-1	-3.281E-3	2.991E-6	1.91E-1	293	223 to 423
SO3	sulfur trioxide	9.510E-1	-3.185E-3	2.789E-6	2.57E-1	293	283 to 483
N2O	nitrous oxide	3.546E-1	-8.952E-4	-1.796E-6	7.67E-2	293	171 to 293
NO	nitric oxide	1.773E-1	1.060E-3	-8.891E-6	1.83E-1	113	110 to 177
NO2	nitrogen dioxide	2.176E-1	2.604E-5	-1.077E-6	1.33E-1	293	262 to 415
H2O	water	-3.838E-1	5.254E-3	-6.369E-6	6.09E-1	293	273 to 623
H2O2	hydrogen peroxide	-1.954E-1	3.374E-3	-3.667E-6	4.79E-1	293	273 to 673
NH3	ammonia	1.068E+0	-1.577E-3	-1.229E-6	5.00E-1	293	196 to 373
N2H4	hydrazine	1.198E+0	-7.337E-4	-1.017E-6	8.95E-1	293	275 to 591

Formula	Name	A	B	C	λ	T	Range
CH$_4$	methane	3.026E-1	-6.047E-4	-3.197E-6	1.35E-1	153	90 to 183
C$_2$H$_6$	ethane	2.928E-1	-6.945E-4	-2.039E-7	7.17E-2	293	90 to 293
C$_3$H$_8$	propane	2.611E-1	-5.309E-4	-8.876E-8	9.78E-2	293	85 to 353
C$_2$H$_4$	ethylene	3.565E-1	-9.586E-4	-1.972E-7	1.46E-1	210	104 to 269
C$_3$H$_6$	propylene	2.906E-1	-6.053E-4	1.256E-8	1.14E-1	293	88 to 343
C$_4$H$_8$	1-butene	2.554E-1	-3.984E-4	-1.135E-7	1.29E-1	293	88 to 393
C$_4$H$_8$	isobutylene	2.325E-1	-5.204E-4	2.609E-7	1.02E-1	293	133 to 373
C$_4$H$_6$	1,3-butadiene	3.007E-1	-7.837E-4	4.916E-7	1.13E-1	293	164 to 393
C$_5$H$_8$	isoprene	2.215E-1	-3.170E-4	-5.527E-8	1.24E-1	293	127 to 433
C$_6$H$_6$	benzene	1.776E-1	4.773E-6	-3.781E-7	1.47E-1	293	278 to 533
C$_7$H$_8$	toluene	2.031E-1	-2.254E-4	-2.470E-8	1.35E-1	293	178 to 581
C$_8$H$_{10}$	ethyl benzene	2.142E-1	-3.440E-4	1.943E-7	1.30E-1	293	178 to 573
C$_8$H$_{10}$	o-xylene	1.649E-1	-7.440E-5	-1.415E-7	1.31E-1	293	248 to 605
C$_8$H$_{10}$	m-xylene	1.643E-1	-1.466E-5	-2.387E-7	1.39E-1	293	225 to 603
C$_8$H$_{10}$	p-xylene	1.487E-1	2.717E-5	-2.822E-7	1.32E-1	293	287 to 609
C$_8$H$_8$	styrene	2.696E-1	-3.384E-4	1.675E-8	1.72E-1	293	243 to 623
C$_9$H$_{12}$	cumene	1.973E-1	-2.421E-4	2.052E-8	1.28E-1	293	180 to 578
C$_{10}$H$_8$	naphthalene	1.328E-1	5.954E-5	-1.692E-7	1.30E-1	393	354 to 733
C$_3$H$_6$	cyclopropane	1.661E-1	-1.763E-4	-2.814E-7	9.03E-2	293	146 to 390
C$_4$H$_8$	cyclobutane	1.452E-1	-1.217E-4	-1.516E-7	9.64E-2	293	183 to 435
C$_5$H$_{10}$	cyclopentane	2.143E-1	-2.588E-4	-5.820E-8	1.33E-1	293	180 to 488
C$_6$H$_{12}$	cyclohexane	1.626E-1	-9.513E-5	-1.382E-7	1.23E-1	293	267 to 527
CH$_3$OH	methanol	3.225E-1	-4.785E-4	1.168E-7	1.92E-1	293	176 to 483
C$_2$H$_5$OH	ethanol	2.629E-1	-3.847E-4	2.211E-7	1.69E-1	293	160 to 463
C$_3$H$_7$OH	n-propanol	1.854E-1	-3.366E-5	-2.215E-7	1.56E-1	293	148 to 493
C$_4$H$_9$OH	n-butanol	2.288E-1	-2.697E-4	1.323E-8	1.51E-1	293	184 to 503

TABLE 10-5 Thermal Conductivities of Some Liquids[1] (*Continued*)

$\lambda = A + BT + CT^2$, λ in W/(m·K) and T in kelvins

Formula	Name	A	B	C	λ	T	Range
C_2H_4O	ethylene oxide	2.624E-1	-3.329E-4	-1.193E-7	1.55E-1	293	161 to 453
C_3H_7O	propylene oxide	2.359E-1	-2.236E-4	-2.127E-7	1.52E-1	293	162 to 453
C_4H_9O	butylene oxide	2.146E-1	-1.196E-4	-3.057E-7	1.53E-1	293	123 to 513
$C_6H_5NH_2$	aniline	2.251E-1	-1.274E-4	-6.239E-8	1.82E-1	293	268 to 680
CH_3Cl	methyl chloride	3.781E-1	-6.639E-4	-1.763E-7	1.68E-1	293	176 to 396
CH_2Cl_2	methylene chloride	2.252E-1	-2.532E-4	-1.126E-7	1.41E-1	293	177 to 459
$CHCl_3$	chloroform	1.634E-1	-8.617E-5	-2.119E-7	1.20E-1	293	210 to 510
CCl_4	carbon tetrachloride	1.608E-1	-1.903E-4	-1.005E-8	1.04E-1	293	250 to 497
C_6H_5Cl	chlorobenzene	1.809E-1	-1.604E-4	-4.689E-8	1.30E-1	293	228 to 600
C_4H_5Cl	chloroprene	1.925E-1	-3.439E-4	1.491E-7	1.04E-1	293	143 to 493

1. Miller, J.W. Jr., J.J. McGinley, and C.L. Yaws, *Chem. Eng.* **83** (23), 133 (1976).

To date, theory has not been successful in formulating useful and accurate expressions to calculate liquid thermal conductivities; approximate techniques must be employed for engineering applications.

Only relatively simple organic liquids are considered in the sections to follow. Ho et al. [55] have presented a comprehensive review covering the thermal conductivity of the elements, and Ewing et al. [41] and Gambill [46] consider, respectively, molten metals and molten salt mixtures. Cryogenic liquids are discussed by Preston et al. [128] and Mo and Gubbins [109].

10-9 Estimation of the Thermal Conductivities of Pure Liquids

All estimation techniques for the thermal conductivity of pure liquids are empirical; and with only limited examination, they often appear rather accurate. As noted earlier, however, below the normal boiling point, the thermal conductivities of most organic, nonpolar liquids lie between 0.10 and 0.17 W/(m·K). With this fact in mind, it is not too difficult to devise various schemes for estimating λ_L within this limited domain.

Many estimation methods were tested; three of the better ones are described below. Others that were considered are noted briefly at the end of the section.

Latini et al. method

In an examination of the thermal conductivities of many diverse liquids, Latini and his coworkers suggest a correlation of the form [1, 2, 4, 5, 6, 7, 77]:

$$\lambda_L = \frac{A(1 - T_r)^{0.38}}{T_r^{1/6}} \tag{10-9.1}$$

where λ_L = thermal conductivity of the liquid, W/(m·K)
$\quad T_b$ = normal boiling temperature (at 1 atm), K
$\quad T_c$ = critical temperature, K
$\quad M$ = molecular weight, g/mol
$\quad T_r = T/T_c$
$$A = \frac{A^* T_b^\alpha}{M^\beta T_c^\gamma} \tag{10-9.2}$$

and the parameters A^*, α, β, and γ are shown in Table 10-6 for various classes of organic compounds. Specific values of A are given for many compounds in [5]. Equation (10-9.2) is only an approximation of the regressed value of A, and this simplification introduces significant error unless $50 < M < 250$.

TABLE 10-6   Latini et al. Correlation Parameters for Eq. (10-9.2)

Family	A^*	α	β	γ
Saturated hydrocarbons	0.00350	1.2	0.5	0.167
Olefins	0.0361	1.2	1.0	0.167
Cycloparaffins	0.0310	1.2	1.0	0.167
Aromatics	0.0346	1.2	1.0	0.167
Alcohols	0.00339	1.2	0.5	0.167
Acids (organic)	0.00319	1.2	0.5	0.167
Ketones	0.00383	1.2	0.5	0.167
Esters	0.0415	1.2	1.0	0.167
Ethers	0.0385	1.2	1.0	0.167
Refrigerants				
R20, R21, R22, R23	0.562	0.0	0.5	−0.167
Others	0.494	0.0	0.5	−0.167

Some estimated values of λ_L found from Eqs. (10-9.1) and (10-9.2) are compared with experimental results in Table 10-7. Errors vary, but they are usually less than 10 percent. Many types of compounds (e.g., nitrogen- or sulfur-containing materials and aldehydes) cannot be treated, and problems arise if the compound may be fitted into two families. *m*-Cresol (Table 10-7) is an example. It could be considered an aromatic compound or an alcohol. In this case, we chose it to be an aromatic material, but the error would not have been very different if it had been considered an alcohol.

Boiling-point method

Sato [90] suggested that, at the normal boiling point,

$$\lambda_L (T_b) = \frac{1.11}{M^{1/2}} \tag{10-9.3}$$

where $\lambda_L (T_b)$ = the thermal conductivity of the liquid at the normal boiling point (at 1 atm), W/(m·K)

M = molecular weight, g/mol

To estimate λ_L at other temperatures, the Riedel equation [135] may be used

$$\lambda_L = B[3 + 20(1 - T_r)^{2/3}] \tag{10-9.4}$$

so, combining Eqs. (10-9.3) and (10-9.4),

$$\lambda_L = \frac{(1.11/M^{1/2})[3 + 20(1 - T_r)^{2/3}]}{3 + 20(1 - T_{br})^{2/3}} \tag{10-9.5}$$

TABLE 10-7 Comparison between Calculated and Experimental Values of Liquid Thermal Conductivity

All values of λ_L are in W/(m·K)

Compound	T, K	λ_L, exp.	Latini et al.	Sato and Riedel	Missenard and Riedel
			Percent error† calculated by the method of		
Propane	323	0.0783	−19	27	18
n-Pentane	293	0.114	−5.7	20	17
	303	0.111	−5.9	20	17
n-Decane	314	0.127	−3.2	−2.0	9.5
	349	0.119	−2.9	−1.8	9.8
Cyclohexane	293	0.124	−1.2	11	3.7
Methylcyclopentane	293	0.121	−3.2	13	3.8
	311	0.115	−2.2	14	4.7
Benzene	293	0.148	0	−3.4	−5.1
	323	0.137	1.9	−2.1	−4.0
	389	0.114	5.1	0	−1.8
Ethylbenzene	293	0.132	2.0	2.2	4.4
	353	0.118	2.9	3.2	5.3
Ethanol	293	0.165	−3.3	15	24
	313	0.152	0	19	28
	347	0.135	3.5	22	32
n-Octanol	293	0.166	−11	−19	5.6
t-Butyl alcohol	311	0.116	4.5	26	77
m-Cresol	293	0.150	10	−3.6	28
	353	0.145	3.8	−8.6	21
Aniline	290	0.178	—	−15	10
Propionic acid	285	0.173	−8.9	−3.4	15
Methylene chloride	253	0.159	−17	−13	−6.3
	293	0.148	−19	−15	−7.9
Carbon tetrachloride	253	0.110	−6.4	−0.8	15
	293	0.103	−7.3	−1.6	14
Ethyl bromide	293	0.103	2.0	7.7	−6.9
Chlorobenzene	233	0.141	−0.5	0	2.6
	353	0.111	2.4	4.1	7.1
Iodobenzene	253	0.106	−15	−0.4	5.1
	353	0.0938	−17	−0.9	4.5
Ethyl acetate	293	0.147	2.9	−7.1	3.1
	333	0.141	2.4	−12	−2.7
Butyl acetate	293	0.137	2.5	−4.9	9.2
Acetone	273	0.171	−9.8	−2.2	3.7
	313	0.151	−6.9	0.5	6.6
Diethyl ether	293	0.129	3.9	4.5	22
Acetaldehyde	293	0.190	—	−12	−11

†Percent error = [(calc. − exp.)/exp.] × 100
Experimental values of the thermal conductivity were obtained from Refs. 19, 36, 65, and 173.

Equation (10-9.5) was employed to estimate λ_L values in Table 10-7. The data required are T, T_c, T_b, and M. Errors varied widely. Poor results were found for low-molecular-weight hydrocarbons and branched hydrocarbons; generally the predicted value was larger than the experimental value. Better results were obtained for nonhydrocarbons.

Method of Missenard

Missenard has suggested several methods to estimate the thermal conductivity of organic liquids. In one [108], he proposed that

$$\lambda_L = \frac{C(DT_b - T)}{(DT_b - E)} \tag{10-9.6}$$

where C, D, and E were evaluated for several organic families. T_b is the normal boiling point. In another technique [105], he recommended

$$\lambda_L (273 \text{ K}) = \frac{(9.0 \times 10^{-3})(T_b \rho'/M)^{1/2} C'_p}{N^{1/4}} \tag{10-9.7}$$

where λ_L (273 K) = liquid thermal conductivity at 273 K, W/(m·K)
$\quad\quad\quad\quad T_b$ = normal boiling temperature (at 1 atm), K
$\quad\quad\quad\quad \rho'$ = liquid density, mol/cm^3 at 273 K
$\quad\quad\quad\quad C'_p$ = liquid heat capacity at constant pressure at 273 K, J/(mol·K)
$\quad\quad\quad\quad M$ = molecular weight, g/mol
$\quad\quad\quad\quad N$ = number of atoms in the molecule

When this equation is combined with Eq. (10-9.4), one obtains

$$\lambda_L = \frac{\lambda_L (273 \text{ K}) [3 + 20(1 - T_r)^{2/3}]}{3 + 20[1 - (273/T_c)]^{2/3}} \tag{10-9.8}$$

Equation (10-9.8) with λ_L (273 K) from Eq. (10-9.7) was used to calculate values for Table 10-7. In almost all cases, the estimated λ_L exceeded the experimentally reported value. The constant 9.0×10^{-3} in Eq. (10-9.7) should, perhaps, be decreased by 10 to 15 percent. In fact, Missenard did suggest a change to 8.4×10^{-3} [104].

Other liquid thermal conductivity estimation techniques

For nonpolar materials, the estimation procedures in Sec. 10-5 may be employed to obtain λ_L when temperatures are well above the normal boiling point and accurate fluid densities are available. In particular, the Chung et al. and Ely and Hanley methods were specifically devised to

treat liquid systems at high reduced temperatures as well as high-pressure gases.

Teja and Rice [161, 162] have suggested that, in some cases, values of λ_L are available for compounds similar to the one of interest, and these data could be employed in an interpolative scheme as follows. Two liquids, similar chemically and with acentric factors bracketing the liquid of interest, are selected. The liquid thermal conductivities of these *reference* liquids should be known over the range of *reduced temperatures* of interest. We denote the properties of one reference fluid by a prime and the other by a double prime. Defining

$$\phi = \frac{V_c^{2/3} M^{1/2}}{T_c^{1/2}} \qquad (10\text{-}9.9)$$

then $\lambda_L \phi$ is found by an interpolation based on the acentric factor ω as shown in Fig. 10-9.

$$\lambda_L \phi = (\lambda_L \phi)' + \frac{\omega - \omega'}{\omega'' - \omega'} [(\lambda_L \phi)'' - (\lambda_L \phi)'] \qquad (10\text{-}9.10)$$

In Eq. (10-9.10) when one selects λ'_L and λ''_L, they should be evaluated at the same reduced temperature as for the compound of interest. The procedure is illustrated in Example 10-9.

Mathur et al. [99] developed a correlation for the thermal conductivity of hydrocarbons as a function of the reduced temperature, critical compressibility factor, and the fluid reduced volume as well as the reduced volume at the freezing point. The procedure is applicable to both light and heavy hydrocarbons, and tests indicated errors of only about 5 to 8 percent. Ogiwara et al. [119] suggested a general estimation relation for
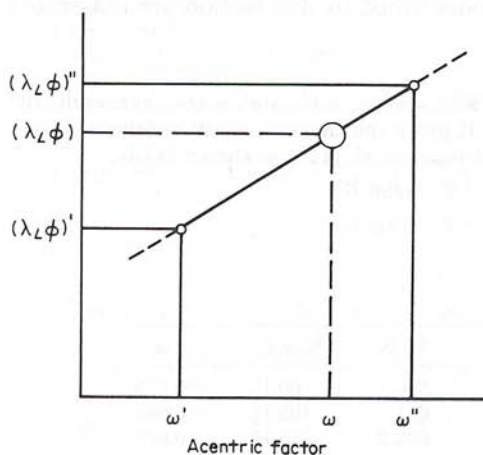
Figure 10-9 Schematic representation of the Teja and Rice interpolation procedure. At the circle, $\lambda_L \phi = (\lambda_L \phi)' + [(\omega - \omega')/(\omega'' - \omega')] [(\lambda_L \phi)'' - (\lambda_L \phi)']$.

λ_L for aliphatic alcohols. Jamieson [58] and Jamieson and Cartwright [60] proposed a general equation to correlate λ_L over a wide temperature range (see Sec. 10-10), and they discuss how the constants in their equation vary with structure and molecular size. New liquid thermal conductivity data were reported for alcohols [58, 60, 119], alkyl amines [58, 60], esters [24], hydrocarbons [115, 118], and nitroalkanes [61].

Discussion and recommendations

The brief comparison shown in Table 10-7 between experimental and estimated values of liquid thermal conductivity would indicate that the Latini et al. and Sato-Riedel methods are somewhat more reliable than the method of Missenard-Riedel, but there are exceptions. A comprehensive testing of the Sato-Riedel form by Baroncini et al. [3] indicated it also was a reasonably accurate estimation method. In many instances, the experimental data are not believed to be particularly reliable and the estimation errors are in the same range as the experimental uncertainity. This is clearly evident from the careful survey of liquid thermal conductivity data provided by the National Engineering Laboratory [58, 60, 65].

For *organic* liquids in the temperature region below the normal boiling point, we recommend either the Latini et al. or Sato-Riedel methods. Errors can vary widely, but they are usually less than 15 percent. There are very few reliable data for liquid thermal conductivities at reduced temperatures exceeding $T_r = 0.65$, and the relations discussed in this section are generally not recommended. If the liquid is nonpolar and is at a reduced temperature greater than about 0.8, one should use the high-pressure fluid correlations given in Sec. 10-5. (The Latini et al. procedure has, however, been applied successfully for refrigerants up to $T_r = 0.9$ [5].) None of the procedures predict the large increase in λ near the critical point. The estimation techniques described in this section are illustrated in Examples 10-9 and 10-10.

Example 10-9   Using the Teja and Rice scheme, estimate the thermal conductivity of liquid t-butyl alcohol at 318 K given the thermal conductivities of n-propanol and n-hexanol reported by Ogiwara et al. [119] as shown below.

n-Propanol $\lambda_L = 0.202 - 1.76 \times 10^{-4} \, T$ W/(m·K)

n-Hexanol $\lambda_L = 0.190 - 1.36 \times 10^{-4} \, T$ W/(m·K)

Solution   From Appendix A:

	V_c, cm³/mol	T_c, K	M, g/mol	ω
n-Propanol	219	536.8	60.10	0.623
n-Hexanol	381	611	102.18	0.560
t-Butyl alcohol	275	506.2	74.12	0.612

Thus, with Eq. (10-9.9),

ϕ (n-propanol) = 12.16

ϕ (n-hexanol) = 21.49

ϕ (t-butyl alcohol) = 16.18

At 318 K, for t-butyl alcohol, T_r = 318/506.2 = 0.629. At this reduced temperature, the appropriate temperature to use for n-propanol is (0.629)(536.8) = 337.6 K, and for n-hexanol it is (0.629)(611) = 384 K. With these, using the Ogiwara et al. correlations,

λ_L (n-propanol) = 0.202 − (1.76 × 10⁻⁴)(337.6) = 0.143 W/(m·K)
λ_L (n-hexanol) = 0.190 − (1.36 × 10⁻⁴)(384) = 0.138 W/(m·K)

Then, using Eq. (10-9.10) with n-propanol as the ′ reference and n-hexanol as ″ reference,

$$\lambda_L (16.18) = [(0.143)(12.16)] + \frac{0.612-0.623}{0.560-0.623}$$

$$\times [(0.138)(21.49) - (0.143)(12.16)]$$

$$= 1.95$$

$$\lambda_L = \frac{1.95}{16.18} = 0.121 \text{ W/(m·K)}$$

Ogiwara et al. [119] report the experimental value of t-butyl alcohol at 318 K to be 0.128 W/(m·K).

Example 10-10 Estimate the thermal conductivity of carbon tetrachloride at 293 K. At this temperature, Jamieson and Tudhope [65] list 11 values. Six are given a ranking of A and are considered reliable. They range from 0.102 to 0.107 W/(m·K). Most, however, are close to 0.103 W/(m·K).

solution The data (unless otherwise noted from Appendix A) are:

	273 K	293 K
Heat capacity, J/(mol·K) [136]	130.7	132.0
Density, mol/cm³ [136]	0.0106	0.0103
Critical temperature, K	556.4	
Normal boiling point (1 atm)	349.9	
Molecular weight, g/mol	153.823	
Number of atoms, N	5	

LATINI ET AL. Assuming CCl₄ to be a refrigerant, by Eq. (10-9.2) and Table 10-6,

$$A = \frac{0.494(556.4)^{1/6}}{(153.823)^{1/2}} = 0.114$$

Then, with T_r = 293/556.4 = 0.527 and Eq. (10-9.1),

$$\lambda_L = \frac{(0.114)(1 - 0.527)^{0.38}}{(0.527)^{1/6}} = 0.0954 \text{ W/(m·K)}$$

$$\text{Error} = \frac{0.0954 - 0.103}{0.103} \times 100 = -7.4\%$$

SATO-RIEDEL. With Eq. (10-9.5) with $T_r = 0.527$ and $T_{b_r} = 349.9/556.4 = 0.629$, we have

$$\lambda_L = \frac{1.11}{(153.84)^{1/2}} \frac{3 + 20(1 - 0.527)^{2/3}}{3 + 20(1 - 0.629)^{2/3}} = 0.101 \text{ W/(m·K)}$$

$$\text{Error} = \frac{0.101 - 0.103}{0.103} \times 100 = -1.6\%$$

MISSENARD-RIEDEL. First, from Eq. (10-9.7), λ_L (273 K), the thermal conductivity at 273 K is determined:

$$\lambda_L \text{ (273 K)} = (9.0 \times 10^{-3})[(349.9)(0.0106)]^{1/2} \frac{130.7}{(153.84)^{1/2}(5)^{1/4}}$$

$$= 0.122 \text{ W/(m·K)}$$

Then, with Eq. (10-9.8), and $273/556.4 = 0.491$

$$\lambda_L = (0.122) \frac{3 + 20(1 - 0.527)^{2/3}}{3 + 20(1 - 0.491)^{2/3}} = 0.118 \text{ W/(m·K)}$$

$$\text{Error} = \frac{0.118 - 0.103}{0.103} \times 100 = 14\%$$

10-10 Effect of Temperature on the Thermal Conductivities of Liquids

Except for aqueous solutions, water, and some multihydroxy and multi-amine molecules, the thermal conductivities of most liquids decrease with temperature. Below or near the normal boiling point, the decrease is nearly linear and is often represented over small temperature ranges by

$$\lambda_L = A - BT \tag{10-10.1}$$

where A and B are constants and B generally is in the range of 1 to 3 $\times$ 10^{-4} W/(m·K^2). In Fig. 10-10, we show the temperature effect on λ_L for a few liquids. Over wider temperature ranges, the correlation suggested by Riedel and given as Eq. (10-9.4) is preferable. Although not suited for water, glycerol, glycols, hydrogen, or helium, Jamieson [57] indicates that the equation represented well the variation of λ_L with temperature for a wide range of compounds. Although, as noted earlier, few data for λ_L exist over the temperature range from near the melting point to near the critical point, for those that are available, Jamieson [58] has found that neither Eq. (10-10.1) nor Eq. (10-9.4) is suitable, and he recommends

$$\lambda_L = A(1 + B\tau^{1/3} + C\tau^{2/3} + D\tau) \tag{10-10.2}$$

where A, B, C, and D are constants and $\tau = 1 - T_r$. For nonassociating liquids, $C = 1 - 3B$ and $D = 3B$. With these simplifications, Eq. (10-10.2) becomes

$$\lambda_L = A[1 + \tau^{2/3} + B(\tau^{1/3} - 3\tau^{2/3} + 3\tau)] \tag{10-10.3}$$

As an example, in Fig. 10-10, if one fits the data for tributyl amine (a polar, but nonassociating, liquid), to Eq. (10-10.3), approximate values of A and B are $A = 0.0590$ W/(m·K) and $B = 0.875$. Using them, one can show by differentiating Eq. (10-10.3) that $d\lambda_L/dT$ decreases with increasing temperature, although, as is obvious from Fig. 10-10, the change in slope is not large in the temperature region shown. For other materials for which data are available over a quite wide temperature range, Eq. (10-10.3) is clearly preferable to Eq. (10-9.1) or (10-9.4) [59].

For associated liquids, $C = 1-2.6B$ and $D \approx 6.5$ for alcohols and 6.0 for alkyd and dialkyd amines. Correlations for C and D for other types of associated molecules are not available. The constants A and B have been correlated, approximately, with carbon number for several homologous series [58, 60, 61].

For saturated liquids at high pressure, variations of λ_L with temperature should probably be determined by using the high-pressure correlations in Sec. 10-5.

10-11   Effect of Pressure on the Thermal Conductivities of Liquids

At moderate pressures, up to 50 to 60 bar, the effect of pressure on the thermal conductivity of liquids is usually neglected, except near the critical point, where the liquid behaves more like a dense gas than a liquid
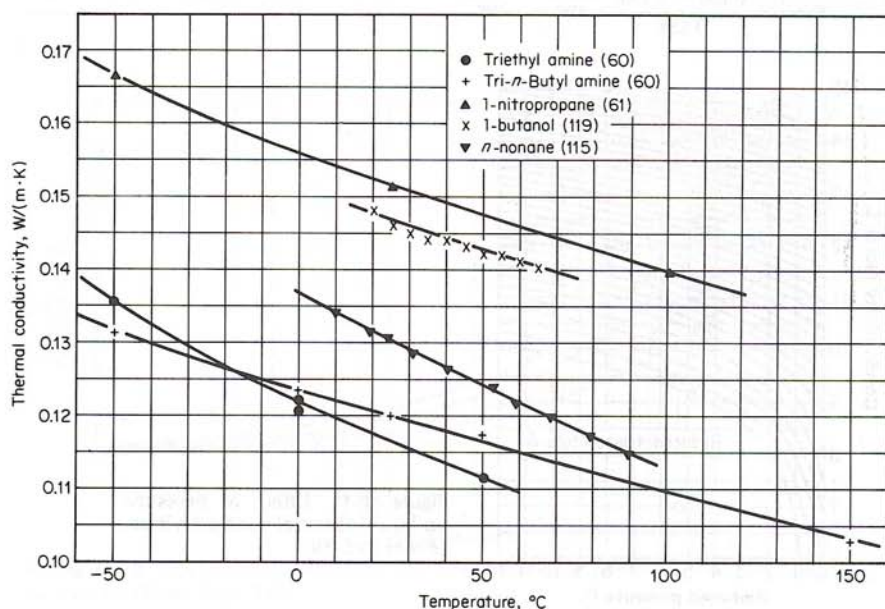
Figure 10-10 Thermal conductivity of a few organic liquids as functions of temperature.

(see Sec. 10-5). At lower temperatures, λ_L increases with pressure. Data showing the effect of pressure on a number of organic liquids are available in Refs. 12 and 64.

A convenient way of estimating the effect of pressure on λ_L is by Eq. (10-11.1).

$$\frac{\lambda_2}{\lambda_1} = \frac{L_2}{L_1} \tag{10-11.1}$$

where λ_2 and λ_1 refer to liquid thermal conductivities at T and pressures P_2 and P_1 and L_2 and L_1 are functions of the reduced temperature and pressure, as shown in Fig. 10-11. This correlation was devised by Lenoir [80]. Testing with data for 12 liquids, both polar and nonpolar, showed errors of only 2 to 4 percent. The use of Eq. (10-11.1) and Fig. 10-11 is illustrated in Example 10-11 with liquid NO_2, a material *not* used in developing the correlation.

Example 10-11 Estimate the thermal conductivity of nitrogen dioxide at 311 K and 276 bar. The experimental value quoted is 0.134 W/(m·K) [132]. The value of λ_L for the saturated liquid at 311 K and 2.1 bar is 0.124 W/(m·K) [132].

solution From Appendix A, T_c = 431 K, P_c = 101 bar; thus T_r = 311/431 = 0.722, P_{r_1} = 2.1/101 = 0.021, and P_{r_2} = 276/101 = 2.73. From Fig. 10-11, L_2 = 11.75 and L_1 = 11.17. With Eq. (10-11.1),

$$\lambda_L \ (276 \ \text{bar}) = (0.124)\frac{11.75}{11.17} = 0.130 \ \text{W/(m·K)}$$

$$\text{Error} = \frac{0.130 - 0.134}{0.134} \times 100 = -3\%$$
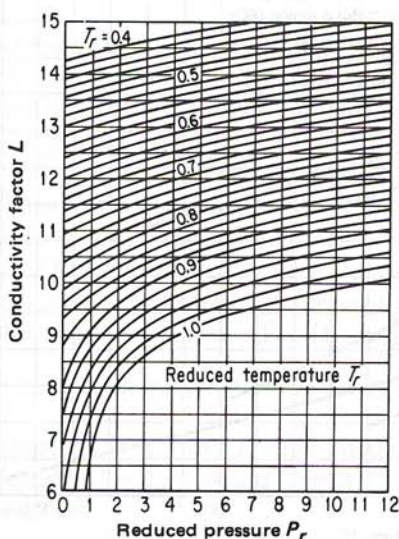
Figure 10-11 Effect of pressure on liquid thermal conductivities. *(From Ref. 80.)*

Missenard [106] has proposed a simple correlation for λ_L that extends to much higher pressures. In analytical form

$$\frac{\lambda_L\,(P_r)}{\lambda_L\,(\text{low pressure})} = 1 + QP_r^{0.7} \tag{10-11.2}$$

$\lambda_L\,(P_r)$ and $\lambda_L\,(\text{low pressure})$ refer to liquid thermal conductivities at high and low, i.e., near saturation, pressure, both at the same temperature. Q is a parameter given in Table 10-8. The correlation is shown in Fig. 10-12.

The correlations of Missenard and Lenoir agree up to a reduced pressure of 12, the maximum value shown for the Lenoir form.

Example 10-12   Estimate the thermal conductivity of liquid toluene at 6330 bar and 304 K. The experimental value at this high pressure is 0.228 W/(m·K) [67]. At 1 bar and 304 K. $\lambda_L = 0.129$ W/(m·K) [67].

TABLE 10-8   Values of Q in Eq. (10-11.2)

	Reduced pressure					
T_r	1	5	10	50	100	200
0.8	0.036	0.038	0.038	(0.038)	(0.038)	(0.038)
0.7	0.018	0.025	0.027	0.031	0.032	0.032
0.6	0.015	0.020	0.022	0.024	0.025	0.025
0.5	0.012	0.0165	0.017	0.019	0.020	0.020
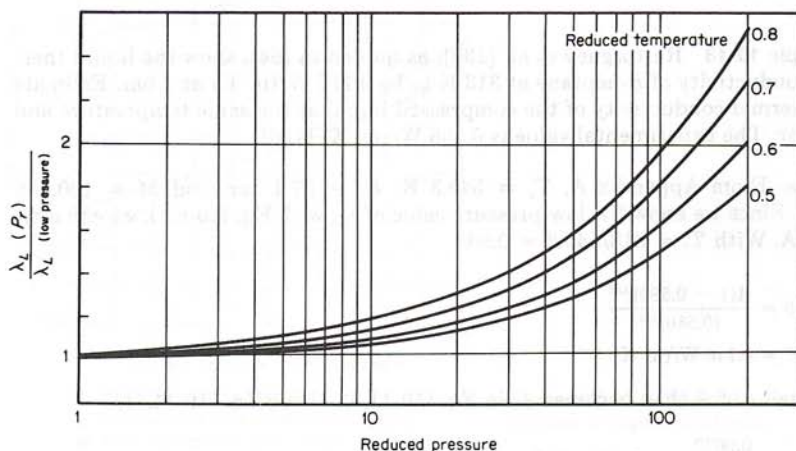
Figure 10-12 Missenard correlation for liquid thermal conductivities at high pressures. *(From Ref. 106.)*

solution From Appendix A, $T_c = 591.8$ K and $P_c = 41.0$ bar. Therefore, $T_r = 304/591.8 = 0.514$ and $P_r = 6330/41.0 = 154$. From Table 10-8, $Q = 0.0205$. Then, using Eq. (10-11.2),

$$\lambda_L (P_r) = (0.129)[1 + (0.0205)(154)^{0.7}] = 0.219 \text{ W/(m·K)}$$

$$\text{Error} = \frac{0.219 - 0.228}{0.228} \times 100 = -4\%$$

Latini and Baroncini [76] correlated the effect of pressure on liquid thermal conductivity by using Eq. (10-9.1), but they expressed the A parameter as

$$A = A_0 + A_1 P_r \tag{10-11.3}$$

Thus, A_0 would represent the appropriate A parameter at low pressures, as described in Sec. 10-9 and given by Eq. (10-9.2). Values of A_1 were found to range from 6×10^{-3} to 6×10^{-4} W/(m·K); thus the term $A_1 P_2$ is negligibly small except at quite high values of P_r. The authors have generalized the parameter A_1 for hydrocarbons as

$$A_1 = \frac{0.0673}{M^{0.84}} \text{ saturated hydrocarbons} \tag{10-11.4}$$

$$A_1 = \frac{102.50}{M^{2.4}} \text{ aromatics} \tag{10-11.5}$$

For hydrocarbons the authors found average errors usually less than 6 percent with maximum errors of 10 to 15 percent. The method should not be used for reduced pressures exceeding 50.

Example 10-13 Rastorguev et al. [130], as quoted in [64], show the liquid thermal conductivity of n-heptane at 313 K to be 0.115 W/(m·K) at 1 bar. Estimate the thermal conductivity of the compressed liquid at the same temperature and 490 bar. The experimental value is 0.136 W/(m·K) [130].

solution From Appendix A, $T_c = 540.3$ K, $P_c = 27.4$ bar, and $M = 100.205$ g/mol. Since we know the low-pressure value of λ_L, with Eq. (10-9.1), we can estimate A. With $T_r = 313/540.3 = 0.580$,

$$0.115 = \frac{A(1 - 0.580)^{0.38}}{(0.580)^{1/6}}$$

$$A = 0.146 \text{ W/(m·K)}$$

This value of A then becomes A_0 in Eq. (10-11.3). Using Eq. (10-11.4),

$$A_1 = \frac{0.0673}{(100.205)^{0.84}} = 1.40 \times 10^{-3}$$

Then, using Eqs. (10-9.1) and (10-11.3) with $P_r = 490/27.4 = 17.9$,

$$\frac{\lambda_L(P_r = 17.9)}{\lambda_L \text{ (low pressure)}} = \frac{A_0 + A_1 P_r}{A_0}$$

$$= \frac{[0.146 + (1.40 \times 10^{-3})(17.9)]}{(0.146)} = 1.17$$

$$\lambda_L \ (P_r = 17.9) = (0.115)(1.17) = 0.135 \ \text{W/(m·K)}$$

$$\text{Error} = \frac{0.135 - 0.136}{0.136} \times 100 = -1\%$$

10-12   Thermal Conductivities of Liquid Mixtures

The thermal conductivities of most mixtures of organic liquids are usually less than those predicted by either a mole or weight fraction average, although the deviations are often small. We show data for several binaries in Fig. 10-13 to illustrate this point.

Many correlation methods for λ_m have been proposed [38, 70, 81, 86, 88, 128, 129, 144, 154, 155, 161, 162, 173, 182]. Five were selected for presentation in this section. They are described separately and evaluated later

- ● Benzene-hexafluorobenzene, 50°C
- ▲ Isobutanol-carbon tetrachloride, 50°C
- ■ Ethyl formate-toluene, 15°C
- + Methanol-acetone, 50°C
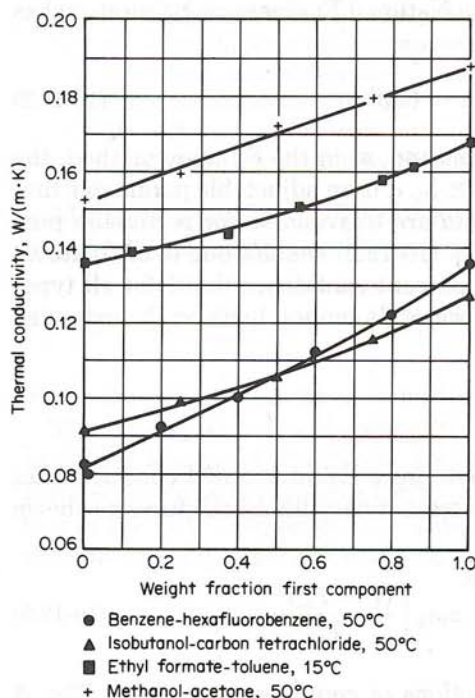
Figure 10-13 Thermal conductivities of liquid mixtures.

when examples are presented to illustrate the methodology in using each of the methods.

There is a surprisingly large amount of experimental mixture data [7, 45, 62, 63, 64, 118, 119, 129, 154, 167], although most are for temperatures near ambient.

Filippov equation

This correlation was developed by researchers in the Soviet Union [42, 43], and it has been extensively tested on many types of mixtures.

$$\lambda_m = w_1\lambda_1 + w_2\lambda_2 - 0.72w_1w_2(\lambda_2 - \lambda_1) \tag{10-12.1}$$

where w_1, w_2 are the weight fractions of components 1 and 2 and λ_1, λ_2 are the pure component thermal conductivities. The components were so chosen that $\lambda_2 \geq \lambda_1$. The constant 0.72 may be replaced by an adjustable parameter if binary mixture data are available. The technique is not suitable for multicomponent mixtures.

Jamieson et al. correlation [64]

Research and data evaluation at the National Engineering Laboratory has suggested, for binary mixtures,

$$\lambda_m = w_1\lambda_1 + w_2\lambda_2 - \alpha(\lambda_2 - \lambda_1)[1 - (w_2)^{1/2}]w_2 \tag{10-12.2}$$

where w_1 and w_2 are weight fractions and, as in the Filippov method, the components are so selected that $\lambda_2 \geq \lambda_1$. α is an adjustable parameter that is set equal to unity if mixture data are unavailable for regression purposes. The authors indicate that Eq. (10-12.2) enables one to estimate λ_m within about 7 percent (with a 95 percent confidence limit) for all types of binary mixtures with or without water. It cannot, however, be extended to multicomponent mixtures.

Baroncini et al. correlation [1, 6, 7]

The Latini et al. method to estimate pure liquid thermal conductivities [Eq. (10-9.1)] has been adapted to treat binary liquid mixtures as shown in Eq. (10-12.3).

$$\lambda_m = \left[x_1^2 A_1 + x_2^2 A_2 + 2.2\left(\frac{A_1^3}{A_2}\right)^{1/2} x_1 x_2 \right] \frac{(1 - T_{rm})^{0.38}}{T_{rm}^{1/6}} \tag{10-12.3}$$

where x_1 and x_2 are the mole fractions of components 1 and 2. The A parameters, introduced in Eq. (10-9.1), can be estimated from Eq. (10-9.2)

and Table 10-6, or they can be calculated from pure component thermal conductivities. (See Example 10-13.) The reduced temperature of the mixture $T_{r_m} = T/T_{c_m}$ where

$$T_{c_m} = x_1 T_{c_1} + x_2 T_{c_2} \tag{10-12.4}$$

with T_{c_1} and T_{c_2} the pure component critical temperatures. The choice of which component is number 1 is made with criterion $A_1 \leq A_2$.

This correlation was tested [7] with over 600 datum points on 50 binary systems including those with highly polar components. The average error found was about 3 percent. The method is not suitable for multicomponent mixtures.

Method of Rowley [140]

In this procedure, the liquid phase is modeled by using a two-liquid theory wherein the energetics of the mixture are assumed to favor local variations in composition. The basic relation assumed by Rowley is

$$\lambda_m = \sum_{i=1}^{n} w_i \sum_{j=1}^{n} w_{ji} \lambda_{ji} \tag{10-12.5}$$

where λ_m = liquid mixture thermal conductivity, $W/(m \cdot K)$
    w_i = weight fraction of component i
    w_{ji} = *local* weight fraction of component j relative to a central molecule of component i
    λ_{ji} = characteristic parameter for the thermal conductivity that expresses the interactions between j and i, $W/(m \cdot K)$

Mass fractions were selected instead of mole fractions in Eq. (10-12.5) because it was found that the *excess* mixture thermal conductivity

$$\lambda_m^{ex} = \lambda_m - \sum_{i=1}^{n} w_i \lambda_i \tag{10-12.6}$$

was more symmetrical when weight fractions were employed.

The two-liquid (or local composition) theory was developed in Chap. 8 to derive several of the liquid activity coefficient-composition models. Rowley develops expressions for w_{ij} and relates this quantity to parameters in the NRTL equation (see Table 8-3). In his treatment, he was able to show that Eq. (10-12.5) could be expressed as

$$\lambda_m = \sum_{i=1}^{n} w_i \frac{\sum_{j=1}^{n} w_j G_{ji} \lambda_{ji}}{\sum_{k=1}^{n} w_k G_{ki}} \tag{10-12.7}$$

where G_{ji} and G_{ij} (or G_{ki} and G_{ik}) are the *same* NRTL parameters as used in activity coefficient correlations for the system of interest.

To obtain λ_{ji} ($=\lambda_{ij}$), Rowley makes the important assumption that for any binary, say 1 and 2, $\lambda_m = \lambda_{12} = \lambda_{21}$ when the local *mole fractions* are equal, that is, $x_{12} = x_{21}$. Then, after some algebra, the final correlation is obtained.

$$\lambda_m = \sum_{i=1}^{n} w_i \lambda_i + \sum_{i=1}^{n} w_i \frac{\sum_{j=1}^{n} w_j G_{ji}(\lambda_{ji} - \lambda_i)}{\sum_{k=1}^{n} w_k G_{ki}} \tag{10-12.8}$$

with

$$\lambda_{ij} = \lambda_{ji} = \frac{w_{ij}^* w_{ij}^* \lambda_i + w_{ji}^* w_{ji}^* \lambda_j}{w_{ij}^* w_{ij}^* + w_{ji}^* w_{ji}^*} \tag{10-12.9}$$

$$w_{iij}^* = \frac{w_{ij}^*}{\sum_{k=1}^{n} w_{ki}^* G_{ki}} \tag{10-12.10}$$

$$w_{ij}^* = \frac{M_i (G_{ji})^{1/2}}{M_i (G_{ji})^{1/2} + M_j (G_{ij})^{1/2}} \tag{10-12.11}$$

w_{ji}^* and w_{ji}^* are defined in a similar manner with the i, j subscripts interchanged. Note also that $G_{ii} = G_{jj} = 1$.

For a binary system of 1 and 2, Eqs. (10-12.8) to (10-12.11) become, after some simplification,

$$\lambda_m = w_1 \lambda_1 + w_2 \lambda_2 + w_1 w_2 (\lambda_2 - \lambda_1) R \tag{10-12.12}$$

$$R = \frac{G_{21}}{(w_2 G_{21} + w_1)(1 + Y)} - \frac{G_{12}}{(w_2 + w_1 G_{12})(1 + Y^{-1})} \tag{10-12.13}$$

$$Y = \left(\frac{w_{12}^*}{w_{21}^*}\right)^2 \frac{w_{12}^* G_{12} + w_{21}^*}{w_{12}^* + w_{21}^* G_{21}} \tag{10-12.14}$$

$$w_{12}^* = \frac{M_1 G_{21}^{1/2}}{M_1 G_{21}^{1/2} + M_2 G_{12}^{1/2}} \tag{10-12.15}$$

$$w_{21}^* = 1 - w_{12}^* \tag{10-12.16}$$

When the Rowley correlation is written in the form of Eq. (10-12.12), it is clear that the entire nonideal effect is included in the R parameter, and the form is quite similar to the Filippov and Jamieson et al. relations described earlier.

To employ this technique, values for the liquid thermal conductivities of all pure components are required. In addition, from data sources or from regressing vapor-liquid equilibrium data, the NRTL parameters, G_{ij} and G_{ji} must be found. The concept of relating transport and thermody-

namic properties is an interesting one and bears further study; Brulé and Starling [18] also have advocated such an approach. Rowley's method was devised to treat multicomponent mixtures, although, to date, most of the testing has been on binary systems.

Li method [82]

In another technique developed for multicomponent systems, Li proposed

$$\lambda_m = \sum_{i=1}^{n} \sum_{j=1}^{n} \phi_i \phi_j \lambda_{ij} \qquad (10\text{-}12.17)$$

with

$$\lambda_{ij} = 2(\lambda_i^{-1} + \lambda_j^{-1})^{-1} \qquad (10\text{-}12.18)$$

$$\phi_i = \frac{x_i V_i}{\sum\limits_{j=1}^{n} x_j V_j} \qquad (10\text{-}12.19)$$

x_i is the mole fraction of component i, and ϕ_i is the superficial volume fraction of i. V_i is the molar volume of the pure liquid. For a binary system of 1 and 2, Eq. (10-12.17) becomes

$$\lambda_m = \phi_1^2 \lambda_1 + 2\phi_1 \phi_2 \lambda_{12} + \phi_2^2 \lambda_2 \qquad (10\text{-}12.20)$$

The harmonic mean approximation for λ_{ij} was chosen over a geometric or arithmetic mean after extensive testing and comparison of calculated and experimental values of λ_m. Also, it was found that the V_i terms in Eq. (10-12.19) could be replaced by critical volumes for nonaqueous liquid systems without affecting the results significantly.

Discussion

All five methods for estimating λ_m described in this section have been extensively tested by using binary mixture data, and all show approximately the same average error [182]. All require the thermal conductivities of the pure components making up the system (or an estimate of the values), and thus they are interpolative in nature. The Filippov and Jamieson et al. procedures require no addition information for a binary other than the weight fractions and pure component values of λ_L. The Baroncini et al. method also needs pure component critical properties, and Li's technique utilizes liquid volumes. Rowley's correlation requires the NRTL parameters G_{ij} and G_{ji} from phase equilibrium data. Only Li's and Rowley's methods will treat multicomponent mixtures. In Fig. 10-14 we show some recent measurements of Usmanov and Salikov for very polar systems and illustrate how well Filippov's relation (10-12.1) fits
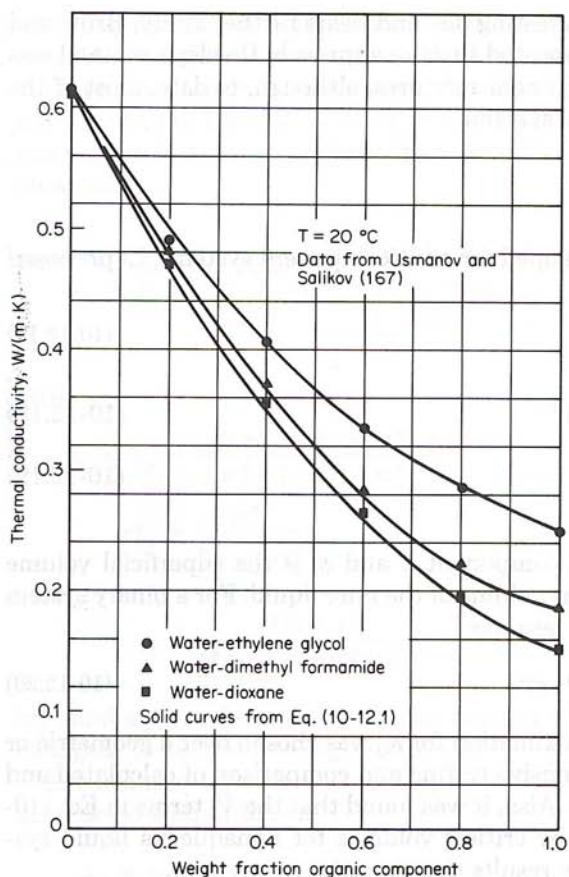
Figure 10-14 Filippov correlation of liquid mixture thermal conductivity.

these data. The other methods described in this section would have been equally satisfactory. Gaitonde et al. [45] measured λ_m for liquid mixtures of alkanes and silicone oils to study systems with large differences in the molecular sizes of the components. They found the Filippov and Jamieson et al. correlations provide a good fit to the data, but they recommended the general form of McLaughlin [88] with the inclusion of an adjustable binary parameter.

In summary, one can use any of the relations described in this section to estimate λ_m with the expectation that errors will rarely exceed about 5 percent.

In the case of aqueous *(dilute)* solutions containing electrolytes, the mixture thermal conductivity usually decreases with an increase in the concentration of the dissolved salts. To estimate the thermal conductivity

of such mixtures, Jamieson and Tudhope [65] recommend the use of an equation proposed originally by Riedel [135] and tested by Vargaftik and Os'minin [172]. At 293 K:

$$\lambda_m = \lambda \, (H_2O) + \Sigma \, \sigma_i C_i \tag{10-12.21}$$

where λ_m = thermal conductivity of the ionic solution at 293 K, $W/(m \cdot K)$
$\lambda \, (H_2O)$ = thermal conductivity of water at 293 K, $W/(m \cdot K)$
C_i = concentration of the electrolyte, mol/L
σ_i = coefficient that is characteristic for each ion

Values of σ_i are shown in Table 10-9. To obtain λ_m at other temperatures,

$$\lambda_m \, (T) = \lambda_m \, (293) \frac{\lambda \, (H_2O \text{ at } T)}{\lambda \, (H_2O \text{ at } 293 \text{ K})} \tag{10-12.22}$$

Except for strong acids and bases at high concentrations, Eqs. (10-12.21) and (10-12.22) are usually accurate to within ±5 percent.

Example 10-14 Using Filippov's, Jamieson et al.'s, and Li's methods, estimate the thermal conductivity of a liquid mixture of methanol and benzene at 273 K. The weight fraction methanol is 0.4. At this temperature, the thermal conductiv-

TABLE 10-9 Values of σ_i for Anions and Cations in Eq. (10-12.21) [65]

Anion	$\sigma_i \times 10^5$	Cation	$\sigma_i \times 10^5$
OH^-	20.934	H^+	-9.071
F^-	2.0934	Li^+	-3.489
Cl^-	-5.466	Na^+	0.000
Br^-	-17.445	K^+	-7.560
I^-	-27.447	NH_4^+	-11.63
NO_2^-	-4.652	Mg^{2+}	-9.304
NO_3^-	-6.978	Ca^{2+}	-0.5815
ClO_3^-	-14.189	Sr^{2+}	-3.954
ClO_4^-	-17.445	Ba^{2+}	-7.676
BrO_3^-	-14.189	Ag^+	-10.47
CO_3^{2-}	-7.560	Cu^{2+}	-16.28
SiO_3^{2-}	-9.300	Zn^{2+}	-16.28
SO_3^{2-}	-2.326	Pb^{2+}	-9.304
SO_4^{2-}	1.163	Co^{2+}	-11.63
$S_2O_3^{2-}$	8.141	Al^{3+}	-32.56
CrO_4^{2-}	-1.163	Th^{4+}	-43.61
$Cr_2O_7^{2-}$	15.93		
PO_4^{3-}	-20.93		
$Fe(CN)_6^{4-}$	18.61		
Acetate$^-$	-22.91		
Oxalate^{2-}	-3.489		

ities of pure benzene and methanol are 0.152 and 0.210 W/(m·K) [62], respectively. The experimental mixture value is 0.170 W/(m·K).

solution FILIPPOV'S METHOD.   We use Eq. (10-12.1). Here methanol is component 2, since λ (methanol) $> \lambda$ (benzene). Thus,

$$\lambda_m = (0.6)(0.152) + (0.4)(0.210) - (0.72)(0.6)(0.4)(0.210 - 0.152) = 0.165 \text{ W/(m·K)}$$

$$\text{Error} = \frac{0.165 - 0.170}{0.170} \times 100 = -3\%$$

JAMIESON ET AL. METHOD.   Again methanol is chosen as component 2. With Eq. (10-12.2) and $\alpha = 1$,

$$\lambda_m = (0.6)(0.152) + (0.4)(0.210) - (0.210 - 0.152)[1 - (0.4)^{1/2}](0.4)$$

$$= 0.167 \text{ W/(m·K)}$$

$$\text{Error} = \frac{0.167 - 0.170}{0.170} \times 100 = -2\%$$

LI METHOD.   With Eq. (10-12.18),

$$\lambda_{12} = 2[(0.152)^{-1} + (0.210)^{-1}]^{-1} = 0.176 \text{ W/(m·K)}$$

At 273 K, V (methanol) = 39.6 cm³/mol and V (benzene) = 88.9 cm³/mol. If the weight fraction methanol in the mixture is 0.4, the mole fraction is 0.619. Then, with Eq. (10-12.19),

$$\phi \text{ (methanol)} = \frac{(0.619)(39.6)}{(0.619)(39.6) + (0.391)(88.9)}$$

$$= 0.414$$

$$\phi \text{ (benzene)} = 1 - 0.414 = 0.586$$

Using Eq. (10-12.20),

$$\lambda_m = (0.414)^2(0.210) + (0.586)^2(0.152) + (2)(0.414)(0.586)(0.176)$$

$$= 0.174 \text{ W/(m·K)}$$

$$\text{Error} = \frac{0.174 - 0.170}{0.170} \times 100 = 2\%$$

Example 10-15 Estimate the liquid thermal conductivity of a mixture of benzene (1) and methyl formate (2) at 323 K by using the method of Baroncini et al. At this temperature, the values of λ_L for the pure components are $\lambda_1 = 0.138$ and $\lambda_2 = 0.179$ W/(m·K) [7].

solution We will estimate the values of λ_m at 0.25, 0.50, and 0.75 weight fraction benzene. First, however, we need to determine A_1 and A_2. Although Eq. (10-9.2) and Table 10-6 could be used, it is more convenient to employ the pure component values of λ_L with Eq. (10-9.1). From Appendix A, $T_{c1} = 562.2$ K and $T_{c2} = 487.2$ K, so $T_{r1} = 323/562.2 = 0.575$ and $T_{r2} = 323/487.2 = 0.663$.   Then, with Eq. (10-9.1), for benzene,

$$0.138 = \frac{A_1(1 - 0.575)^{0.38}}{(0.575)^{1/6}} \qquad A_1 = 0.174$$

Similarly $A_2 = 0.252$. [Note that, if Eq. (10-9.2) and Table 10-6 had been used, we would have $A_1 = 0.176$ and $A_2 = 0.236$.]
We have selected components 1 and 2 to agree with the criterion $A_1 \leq A_2$.

Consider first a mixture containing 0.25 weight fraction benzene, i.e., $w_1 = 0.25$ and $w_2 = 0.75$. Then, the mole fractions are $x_1 = 0.204$ and $x_2 = 0.796$. Thus,

$$T_{cm} = (0.204)(562.2) + (0.796)(487.2) = 502.5 \text{ K}$$

$$T_{rm} = \frac{323}{502.5} = 0.643$$

With Eq. (10-12.3),

$$\lambda_m = \left\{ (0.204)^2(0.174) + (0.796)^2(0.252) \right.$$
$$\left. + (2.2) \left[\frac{(0.174)^3}{0.252} \right]^{1/2} (0.204)(0.796) \right\} \frac{(1 - 0.643)^{0.38}}{(0.643)^{1/6}}$$

$$= 0.159 \text{ W/(m·K)}$$

Calculated results for this and other compositions are shown below with the experimental values and percent errors.

Benzene-Methyl Formate Mixtures; $T = 323$ K

Weight fraction benzene	Mole fraction benzene	T_{cm}, K	λ_m, calc., W/(m·K)	λ_m, exp., W/(m·K)	Percent error
0.25	0.204	502.5	0.159	0.158	0.6
0.50	0.435	519.8	0.143	0.151	−5.3
0.75	0.698	539.6	0.135	0.140	−3.6

Example 10-16 Use Rowley's method to estimate the thermal conductivity of a liquid mixture of acetone (1) and chloroform (2) that contains 66.1 weight percent of the former. The temperature is 298 K. As quoted by Jamieson et al. [64], Rodriguez [137] reports $\lambda_1 = 0.161$ W/(m·K), $\lambda_2 = 0.119$ W/(m·K), and for the mixture, $\lambda_m = 0.143$ W/(m·K).

solution First, we need the NRTL parameters for this binary at 298 K. Nagata [114] suggests $G_{12} = 1.360$ and $G_{21} = 0.910$. From Appendix A, $M_1 = 58.08$ and $M_2 = 119.38$ g/mol. Using Eqs. (10-12.15) and (10-12.16),

$$w_{12}^* = \frac{(58.08)(0.910)^{1/2}}{(58.08)(0.910)^{1/2} + (119.38)(1.360)^{1/2}}$$
$$= 0.285$$

$$w_{21}^* = 1 - 0.285 = 0.715$$

With Eqs. (10-12.13) and (10-12.14),

$$Y = \left(\frac{0.285}{0.715} \right)^2 \frac{(0.285)(1.360) + 0.715}{0.285 + (0.715)(0.910)}$$
$$= 0.187$$

$$R = \frac{0.910}{[(0.910)(0.339) + 0.661](1 + 0.187)} - \frac{1.360}{[(0.339 + (0.661)(1.360)](1 + 0.187^{-1})}$$
$$= 0.618$$

Then, with Eq. (10-12.12),

$$\lambda_m = (0.661)(0.161) + (0.339)(0.119) + (0.661)(0.339)(0.119 - 0.161)(0.618)$$

$$= 0.141 \text{ W/(m·K)}$$

$$\text{Error} = \frac{0.141 - 0.143}{0.143} \times 100 = -1\%$$

Notation

A	parameter in Eq. (10-9.1), W/(m·K)
A_{ij}	Wassiljewa coefficient, Eq. (10-6.1)
B_i	parameter in Eq. (10-5.9)
C_i	electrolyte concentration, mol/L, Eq. (10-12.21)
C	heat capacity, J/(mol·K); C_v, at constant volume; C_p, at constant pressure; C_{rot}, due to rotational degrees of freedom; C_{int}, due to internal degrees of freedom; C_{tr}, due to translational motion
C	group contribution constant in Eq. (10-3.15)
D	diffusion coefficient, m^2/s
f	scaling parameter in Eqs. (10-3.24) and (10-5.15)
f_{tr}	translational factor in Eq. (10-3.1)
f_{int}	internal energy factor in Eq. (10-3.1)
F_r	number of degrees of freedom for external rotation
G_1	parameter in Eq. (10-5.7)
G_2	parameter in Eq. (10-5.8)
G_{ij}	NRTL parameter, Eq. (10-12.7)
h	scaling parameter in Eqs. (10-3.25) and (10-5.16)
H	parameter in Eqs. (10-3.31) and (10-5.23)
k	Boltzmann's constant, J/K
L	mean free path, m
L	parameter shown in Fig. 10-11
m	molecular mass, g or kg
M	molecular weight, g/mol
M'	molecular weight, kg/mol unless otherwise noted
M'_m	molecular weight defined in Eq. (10-7.22)
n	number density of molecules, m^{-3}; number of components in a mixture
N	number of atoms in a molecule
N_{Pr}	Prandtl number, $C_p\eta/\lambda M'$
N_0	Avogadro's number
P	pressure, N/m^2 or bar; P_c, critical pressure; P_r, reduced pressure, P/P_c
q	parameter defined in Eq. (10-5.5)

Q parameter in Table 10-8, Fig. 10-12

R gas constant, J/(mol·K)

R parameter in Eq. (10-12.13)

T temperature, K; T_c, critical temperature; T_r, reduced temperature, T/T_c; T^+, reduced temperature parameter in Eqs. (10-3.21) and (10-5.11); T_0, equivalent temperature in Eqs. (10-3.26) and (10-5.17); T_b, normal boiling point (at 1 atm); $T_{b_r} = T_b/T_c$

v molecular velocity, m/s

V molar volume, cm³/mol or m³/mol; V_c, critical volume; V^+, reduced volume parameter in Eq. (10-5.12)

w_i weight fraction of component i

w^* parameter in Eqs. (10-12.10) and (10-12.11)

x_i mole fraction of component i in a liquid mixture

Y parameter in Eq. (10-12.14)

Z compressibility factor PV/RT; Z_c, critical compressibility factor

Z parameter defined under Eq. (10-3.17)

Z_{rot} collision number

GREEK

α parameter defined under Eq. (10-3.17); parameter in Eq. (10-12.2)

β parameter defined under Eq. (10-3.17)

γ C_p/C_v

Γ reduced, inverse thermal conductivity defined in Eq. (10-3.11)

ϵ interaction energy parameter, J; parameter in Eq. (10-6.2)

η viscosity, N·s/m²; η^*, viscosity parameter in Eq. (10-3.30); η_0, viscosity parameter in Eq. (10-3.27); $\eta°$, low-pressure gas viscosity

Θ shape factor in Eqs. (10-3.22) and (10-5.13)

κ association constant, see Table 9-1

λ thermal conductivity, W/(m·K); λ_r, reduced thermal conductivity, $\Gamma\lambda$; λ^*, thermal conductivity parameter in Eq. (10-3.29); λ_0, thermal conductivity parameter in Eq. (10-3.28); $\lambda°$, low-pressure gas thermal conductivity; λ^{**}, thermal conductivity parameter in Eqs. (10-5.22) and (10-7.28); λ_{tr}, monatomic value of thermal conductivity; λ', parameter in Eq. (10-7.12)

μ dipole moment, debye; μ_r, reduced dipole moment defined in Eq. (9-4.11)

ρ molar density, mol/cm³ or mol/m³, ρ_c, critical density; ρ_r, reduced density, ρ/ρ_c; ρ_0, density parameter in Eq. (10-5.18); ρ', liquid density, mol cm³, at 273 K

σ characteristic dimension of the molecule, m or Å; σ_i, ion coefficient in Table 10-9

τ $1 - T_r$

ϕ parameter in Eq. (10-9.9); volume fraction in Eq. (10-12.19)

Φ shape factor in Eqs. (10-3.23) and (10-5.14)

Ψ parameter defined under Eq. (10-3.17)

Ω_v collision integral for viscosity and thermal conductivity; Ω_D, collision integral for diffusion coefficients

ω acentric factor

SUBSCRIPTS

m mixture

L liquid

G gas

SUPERSCRIPTS

ex   excess property

$',\,''$ reference properties

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11

Diffusion Coefficients

11-1 Scope

In Sec. 11-2 we discuss briefly several frames of reference from which diffusion can be related and define the diffusion coefficient. Low-pressure binary gas diffusion coefficients are treated in Secs. 11-3 and 11-4. The pressure and temperature effects on gas-phase diffusion coefficients are covered in Secs. 11-5 and 11-6, respectively. The theory for liquid diffusion coefficients is introduced in Sec. 11-8, and estimation methods for binary liquid diffusion coefficients at infinite dilution are described in Sec. 11-9. Concentration effects are considered in Sec. 11-10 and temperature and pressure effects in Sec. 11-11. Brief comments on diffusion in multicomponent mixtures are made in Secs. 11-7 (gases) and 11-12 (liquids); ionic solutions are covered in Sec. 11-13.

11-2 Basic Concepts and Definitions

The extensive use of the term "diffusion" in the chemical engineering literature is based on an intuitive feel for the concept; i.e., diffusion refers to the net transport of material within a single phase in the absence of mixing (by mechanical means or by convection). Both experiment and theory have shown that diffusion can result from pressure gradients (pressure diffusion), temperature gradients (thermal diffusion), external force fields (forced diffusion), and concentration gradients. Only the last type

is considered in this chapter; i.e., the discussion is limited to diffusion in isothermal, isobaric systems with no external force field gradients.

Even with this limitation, confusion can easily arise unless care is taken to define diffusion fluxes and diffusion potentials, e.g., driving forces, clearly. The proportionality constant between the flux and potential is the *diffusion coefficient,* or *diffusivity.*

Diffusion fluxes

A detailed discussion of diffusion fluxes has been given by Bird et al. [20] and Cussler [47]. Various types originate because different reference frames are employed. The most obvious reference plane is fixed on the equipment in which diffusion is occurring. This plane is designated by RR' in Fig. 11-1. Suppose, in a binary mixture of A and B, that A is diffusing to the left and B to the right. If the diffusion rates of these species are not identical, there will be a net depletion or accumulation of molecules in either side of RR'. To maintain the requirements of an isobaric, isothermal system, bulk motion of the mixture occurs. Net movement of A (as measured in the fixed reference frame RR') then results from both diffusion and bulk flow.

Although many reference planes can be delineated, a plane of *no net mole flow* is normally used to define a diffusion coefficient in binary mixtures. If J_A^M represents a mole flux in a mixture of A and B, J_A^M is then the net mole flow of A across the boundaries of a hypothetical (moving) plane such that the total moles of A and B are invariant on both sides of the plane. J_A^M can be related to fluxes across RR' by

$$J_A^M = N_A - x_A (N_A + N_B) \qquad (11\text{-}2.1)$$

where N_A and N_B are the fluxes of A and B across RR' (relative to the fixed plane) and x_A is the mole fraction of A at RR'. Note that J_A^M, N_A, and N_B are vectorial quantities and a sign convention must be assigned to denote flow directions. Equation (11-2.1) shows that the net flow of A across RR' is due to a diffusion contribution J_A^M and a bulk flow contri-
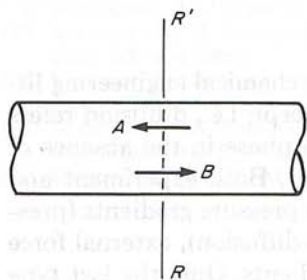
Figure **11-1** Diffusion across plane RR'.

bution $x_A (N_A + N_B)$. For equimolar counterdiffusion, $N_A + N_B = 0$ and $J_A^M = N_A$.

One other flux is extensively used, i.e., one relative to the plane of *no net volume flow*. This plane is less readily visualized. By definition,

$$J_A^M + J_B^M = 0 \tag{11-2.2}$$

and if J_A^V and J_B^V are vectorial molar fluxes of A and B relative to the plane of no net volume flow, then, by definition,

$$J_A^V \overline{V}_A + J_B^V \overline{V}_B = 0 \tag{11-2.3}$$

where $\overline{V}_A$ and $\overline{V}_B$ are the partial molar volumes of A and B in the mixture. It can be shown that

$$J_A^V = \frac{\overline{V}_B}{V} J_A^M \quad \text{and} \quad J_B^V = \frac{\overline{V}_A}{V} J_B^M \tag{11-2.4}$$

where V is the volume per mole of mixture. Obviously, if $\overline{V}_A = \overline{V}_B = V$, as in an ideal-gas mixture, then $J_A^V = J_A^M$.

Diffusion coefficients

Diffusion coefficients for a binary mixture of A and B are defined by

$$J_A^M = -cD_{AB} \frac{dx_A}{dz} \tag{11-2.5}$$

$$J_B^M = -cD_{BA} \frac{dx_B}{dz} \tag{11-2.6}$$

where c is the total molar concentration $(= V^{-1})$ and diffusion is in the z direction. With Eq. (11-2.2), since $(dx_A/dz) + (dx_B/dz) = 0$, we have $D_{AB} = D_{BA}$. The diffusion coefficient then represents the proportionality between the flux of A relative to a plane of no net molar flow and the gradient $c(dx_A/dz)$. From Eqs. (11-2.4) to (11-2.6) and the definition of a partial molar volume it can be shown that, for an isothermal, isobaric binary system,

$$J_A^V = -D_{AB} \frac{dc_A}{dz} \quad \text{and} \quad J_B^V = -D_{AB} \frac{dc_B}{dz} \tag{11-2.7}$$

When fluxes are expressed in relation to a plane of no net volume flow, the potential is the concentration gradient. D_{AB} in Eq. (11-2.7) is identical with that defined in Eq. (11-2.5). In many cases $\overline{V}_A \approx \overline{V}_B \approx V$ (ideal gases, ideal solutions), and in such instances $J_A^V \approx J_A^M$, $J_B^V \approx J_B^M$.

Mutual, self-, and tracer diffusion coefficients

The diffusion coefficient D_{AB} introduced above is termed the *mutual diffusion coefficient,* and it refers to the diffusion of one constituent in a binary system. A similar coefficient D_{1m} would imply the diffusivity of component 1 in a mixture (see Secs. 11-7 and 11-12).

Tracer diffusion coefficients (sometimes referred to as *intradiffusion coefficients*) relate to the diffusion of a labeled component within a *homogeneous* mixture. Like mutual diffusion coefficients, tracer diffusion coefficients can be a function of composition. If D_A^* is the tracer diffusivity of A in a mixture of A and B, then as $x_A \rightarrow 1.0$, $D_A^* \rightarrow D_{AA}$, where D_{AA} is the self-diffusion coefficient of A in pure A.

In Fig. 11-2, the various diffusion coefficients noted above are shown for a binary liquid mixture of *n*-octane and *n*-dodecane at 60°C [216]. In this case, the mutual diffusion of these two hydrocarbons increases as the mixture becomes richer in *n*-octane. With A as *n*-octane and B as *n*-dodecane, as $x_A \rightarrow 1.0$, $D_{AB} = D_{BA} \rightarrow D_{BA}^\circ$, where this notation signifies that this limiting diffusivity represents the diffusion of B in a medium consisting essentially of A, that is, *n*-dodecane molecules diffusing through almost pure *n*-octane. Similarly, D_{AB}° is the diffusivity of A in essentially pure B. Except in the case of infinite dilution, tracer diffusion coefficients differ from binary-diffusion coefficients, and there is no way to relate the two coefficients [47]. Similarly, there is no relation between quantities such as
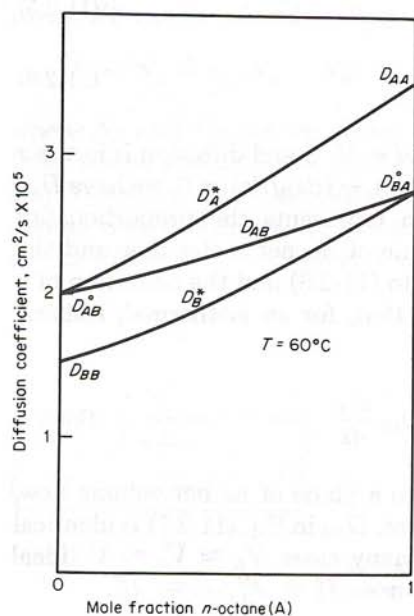
Figure 11-2 Mutual, self-, and tracer diffusion coefficients in a binary mixture of *n*-octane and *n*-dodecane. *(From Ref. 216.)*

D_{BB} and D_{AB}° or D_{AA} and D_{BA}°. In this chapter, only correlation techniques for D_{ij} (or D_{ij}°) are considered; corresponding states methods for D_{ii} have, however, been developed [122, 155].

Chemical potential driving force

The mutual diffusion coefficient D_{AB} in Eq. (11-2.7) indicates that the flux of a diffusing component is proportional to the concentration gradient. Diffusion is, however, affected by more than just the gradient in concentration, e.g., the force fields around molecules [55, 208]. Yet these force fields are some complex function of composition as well as of temperature and pressure. Thus, fluxes should not be expected to be linear in the concentration gradient. Any inadequacy in the defining equation for D_{AB} is reflected by a concentration dependence of experimental diffusion coefficients.

Modern theories of diffusion [75] have adopted the premise that if one perturbs the equilibrium composition of a binary system, the subsequent diffusive flow required to attain a new equilibrium state is proportional to the gradient in chemical potential $(d\mu_A/dz)$. Since the diffusion coefficient was defined in Eqs. (11-2.5) and (11-2.6) in terms of a mole fraction gradient instead of a chemical potential gradient, it is argued that one should include a thermodynamic correction in any equation for D_{AB}. This correction is

$$\alpha = \left[\frac{(\partial \ln a_A)}{(\partial \ln x_A)} \right]_{T,P} \tag{11-2.8}$$

By virtue of the Gibbs-Duhem equation, α is the same regardless of whether activities and mole fractions of either A or B are used in Eq. (11-2.8). For gases, α is almost always close to unity (except at high pressures), and this correction is seldom used. For liquid mixtures, however, it is widely adopted, as will be illustrated in Sec. 11-10.

11-3 Diffusion Coefficients for Binary Gas Systems at Low Pressures: Prediction from Theory

The theory describing diffusion in binary gas mixtures at low to moderate pressures has been well developed. As noted earlier in Chaps. 9 (Viscosity) and 10 (Thermal Conductivity), the theory results from solving the Boltzmann equation, and the results are usually credited to both Chapman and Enskog, who independently derived the working equation

$$D_{AB} = \frac{3}{16} \frac{(4\pi kT/M_{AB})^{1/2}}{n\pi\sigma_{AB}^2\Omega_D} f_D \tag{11-3.1}$$

where M_A, M_B = molecular weights of A and B
$\qquad M_{AB} = 2[(1/M_A) + (1/M_B)]^{-1}$
$\qquad\quad n$ = number density of molecules in the mixture
$\qquad\quad k$ = Boltzmann's constant
$\qquad\quad T$ = absolute temperature

Ω_D, the collision integral for diffusion, is a function of temperature; it depends upon the choice of the intermolecular force law between colliding molecules. σ_{AB} is a characteristic length; it also depends upon the intermolecular force law selected. Finally, f_D is a correction term which is of the order of unity. If M_A is of the same order as M_B, f_D lies between 1.0 and 1.02 regardless of composition or intermolecular forces. Only if the molecular masses are very unequal and the light component is present in trace amounts is the value of f_D significantly different from unity, and even in such cases, f_D is usually between 1.0 and 1.1 [138].

If f_D is chosen as unity and n is expressed by the ideal-gas law, Eq. (11-3.1) may be written as

$$D_{AB} = \frac{0.00266 T^{3/2}}{P M_{AB}^{1/2} \sigma_{AB}^2 \Omega_D} \qquad (11\text{-}3.2)$$

where D_{AB} = diffusion coefficient, cm²/s
$\qquad\quad T$ = temperature, K
$\qquad\quad P$ = pressure, bar
$\qquad\ \sigma_{AB}$ = characteristic length, Å
$\qquad\quad \Omega_D$ = diffusion collision integral, dimensionless

and M_{AB} is defined under Eq. (11-3.1). The key to the use of Eq. (11-3.2) is the selection of an intermolecular force law and the evaluation of σ_{AB} and Ω_D.

Lennard-Jones 12-6 potential

As noted earlier [Eq. (9-4.2)], a popular correlation relating the intermolecular energy ψ between two molecules to the distance of separation r, is given by

$$\psi = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] \qquad (11\text{-}3.3)$$

with ϵ and σ as the characteristic Lennard-Jones energy and length, respectively. Application of the Chapman-Enskog theory to the viscosity of pure gases has led to the determination of many values of ϵ and σ; some of them are given in Appendix B.

To use Eq. (11-3.2), some rule must be chosen to obtain the interaction value σ_{AB} from σ_A and σ_B. Also, it can be shown that Ω_D is a function only

of kT/ϵ_{AB}, where again some rule must be selected to relate ϵ_{AB} to ϵ_A and ϵ_B. The simple rules shown below are usually employed:

$$\epsilon_{AB} = (\epsilon_A\epsilon_B)^{1/2} \tag{11-3.4}$$

$$\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2} \tag{11-3.5}$$

Ω_D is tabulated as a function of kT/ϵ for the 12-6 Lennard-Jones potential [100], and various analytical approximations also are available [92, 109, 112, 158]. The accurate relation of Neufield et al. [158] is

$$\Omega_D = \frac{A}{(T^*)^B} + \frac{C}{\exp(DT^*)} + \frac{E}{\exp(FT^*)} + \frac{G}{\exp(HT^*)} \tag{11-3.6}$$

where $T^* = kT/\epsilon_{AB}$ $A = 1.06036$ $B = 0.15610$

$C = 0.19300$ $D = 0.47635$ $E = 1.03587$

$F = 1.52996$ $G = 1.76474$ $H = 3.89411$

Example 11-1 Estimate the diffusion coefficient for the system N_2-CO_2 at 590 K and 1 bar. The experimental value reported by Ellis and Holsen [61] is 0.583 cm^2/s.

solution To use Eq. (11-3.2), values of σ (CO_2), σ (N_2), ϵ (CO_2), and ϵ (N_2) must be obtained. Using the values in Appendix B with Eqs. (11-3.4) and (11-3.5) gives σ (CO_2) = 3.941 Å, σ (N_2) = 3.798 Å; σ (CO_2-N_2) = (3.941 + 3.798)/2 = 3.8695 Å; ϵ (CO_2)/k = 195.2 K, ϵ (N_2)/k = 71.4 K; ϵ (CO_2-N_2)/k = [(195.2)(71.4)]$^{1/2}$ = 118 K. Then $T^* = kT/\epsilon$ (CO_2-N_2) = 590/118 = 5.0. With Eq. (11-3.6), Ω_D = 0.842. Since M (CO_2) = 44.0 and M (N_2) = 28.0, M_{AB} = (2)[(1/44.0) + (1/28.0)]$^{-1}$ = 34.22. With Eq. (11-3.2),

$$D (CO_2\text{-}N_2) = \frac{(0.00266)(590)^{3/2}}{(1)(34.22)^{1/2}(3.8695)^2(0.842)}$$

$$= 0.52 \; cm^2/s$$

The error is 11 percent. Ellis and Holsen recommend values of ϵ (CO_2-N_2) = 134 K and σ (CO_2-N_2) = 3.660 Å. With these parameters, they predicted D to be 0.56 cm^2/s, a value closer to that found experimentally.

Equation (11-3.2) is derived for dilute gases consisting of nonpolar, spherical, monatomic molecules; and the potential function (11-3.3) is essentially empirical, as are the combining rules [Eqs. (11-3.4) and (11-3.5)]. Yet Eq. (11-3.2) gives good results over a wide range of temperatures and provides useful approximate values of D_{AB} [81, 82]. The general nature of the errors to be expected from this estimation procedure is indicated by the comparison of calculated and experimental values shown later in Table 11-2.

The calculated value of D_{AB} is relatively insensitive to the value of ϵ_{AB} employed and even to the form of the assumed potential function. Values of ϵ and σ are often available from viscosity measurements.

No effect of composition is predicted. A more detailed treatment does indicate that there may be a small effect for cases in which M_A and M_B differ significantly. In a specific study of this effect [234], the low-pressure binary diffusion coefficient for the system He-CClF$_3$ did vary from about 0.416 to 0.430 cm^2/s over the extremes of composition. In another study [154], no effect of concentration was noted for the methyl alcohol–air system, but a small change was observed with chloroform-air.

Low-pressure diffusion coefficients from viscosity data

Since the equations for low-pressure gas viscosity [Eq. (9-3.9)] and diffusion [Eq. (11-3.2)] have a common basis in the Chapman-Enskog theory, they can be combined to relate the two gas properties. Experimental data on viscosity as a function of composition at constant temperature are required as a basis for calculating the *binary* diffusion coefficient D_{AB} [51, 83, 100, 112, 113]. Weissman and Mason [226, 227] compare the method with a large collection of experimental viscosity and diffusion data and find excellent agreement.

Polar gases

If one or both components of a gas mixture are polar, a modified Lennard-Jones relation, such as the Stockmayer potential, is often used. A different collision integral relation [rather than Eq. (11-3.6)] is then necessary, and Lennard-Jones σ and ϵ values are not sufficient.

Brokaw [22] has suggested an alternative method for estimating diffusion coefficients for binary mixtures containing polar components. Equation (11-3.1) is still used, but the collision integral Ω_D is now given as

$$\Omega_D = \Omega_D \, [\text{Eq. (11-3.6)}] + \frac{0.19\delta_{AB}^2}{T^*} \tag{11-3.7}$$

where $T^* = \dfrac{kT}{\epsilon_{AB}}$

and $\delta = \dfrac{1.94 \times 10^3 \, \mu_p^2}{V_b T_b}$ $\qquad$ (11-3.8)

μ_p = dipole moment, debyes

V_b = *liquid* molar volume at the normal boiling point, cm^3/mol

T_b = normal boiling point (1 atm), K

$$\frac{\epsilon}{k} = 1.18(1 + 1.3\delta^2)\,T_b \tag{11-3.9}$$

$$\sigma = \left(\frac{1.585\,V_b}{1 + 1.3\delta^2}\right)^{1/3} \tag{11-3.10}$$

$$\delta_{AB} = (\delta_A \delta_B)^{1/2} \tag{11-3.11}$$

$$\frac{\epsilon_{AB}}{k} = \left(\frac{\epsilon_A}{k}\frac{\epsilon_B}{k}\right)^{1/2} \tag{11-3.12}$$

$$\sigma_{AB} = (\sigma_A \sigma_B)^{1/2} \tag{11-3.13}$$

Note that the polarity effect is related exclusively to the dipole moment; this may not always be a satisfactory assumption [27].

Example 11-2 Estimate the diffusion coefficient for a mixture of methyl chloride (MC) and sulfur dioxide (SD) at 1 bar and 323 K. The data required to use Brokaw's relation are shown below:

	Methyl chloride (MC)	Sulfur dioxide (SD)
Dipole moment, debyes	1.9	1.6
Liquid molar volume at T_b, cm³/mol	50.6	43.8
Normal boiling temperature, K	249.1	263.2

solution With Eqs. (11-3.8) and (11-3.11),

$$\delta\,(\text{MC}) = \frac{(1.94 \times 10^3)(1.9)^2}{(50.6)(249.1)} = 0.55$$

$$\delta\,(\text{SD}) = \frac{(1.94 \times 10^3)(1.6)^2}{(43.8)(263.2)} = 0.43$$

$$\delta\,(\text{MC-SD}) = [(0.55)(0.43)]^{1/2} = 0.49$$

Also, with Eqs. (11-3.9) and (11-3.12),

$$\frac{\epsilon\,(\text{MC})}{k} = 1.18[1 + 1.3(0.55)^2](249.1) = 412\ \text{K}$$

$$\frac{\epsilon\,(\text{SD})}{k} = 1.18[1 + 1.3(0.43)^2](263.2) = 385\ \text{K}$$

$$\frac{\epsilon\,(\text{MC-SD})}{k} = [(412)(385)]^{1/2} = 398\ \text{K}$$

Then, with Eqs. (11-3.10) and (11-3.13),

$$\sigma\,(\text{MC}) = \left[\frac{(1.585)(50.6)}{1 + (1.3)(0.55)^2}\right]^{1/3} = 3.85\ \text{Å}$$

$$\sigma\,(\text{SD}) = \left[\frac{(1.585)(43.8)}{1 + (1.3)(0.43)^2}\right]^{1/3} = 3.82\ \text{Å}$$

$$\sigma\,(\text{MC-SD}) = [(3.85)(3.82)]^{1/2} = 3.84\ \text{Å}$$

To determine Ω_D, $T^* = kT/\epsilon$ (MC-SD) $= 323/398 = 0.811$. With Eq. (11-3.6), $\Omega_D = 1.60$. Then with Eq. (11-3.7),

$$\Omega_D = 1.60 + \frac{(0.19)(0.490)^2}{(0.811)} = 1.65$$

With Eq. (11-3.2) and M (MC) $= 50.49$, M (SD) $= 64.60$, and $M_{AB} = (2)[(1/50.49) + (1/64.60)]^{-1} = 56.68$

$$D_{MC-SD} = \frac{(0.00266)(323)^{3/2}}{(1)(56.68)^{1/2}(3.84)^2(1.65)} = 0.084 \text{ cm}^2/s$$

The experimental value is 0.078 cm²/s and the error is 8 percent.

Discussion

A comprehensive review of the theory and experimental data for gas diffusion coefficients is available [138]. There have been many studies covering wide temperature ranges, and the applicability of Eq. (11-3.1) is well verified. Most investigators select the Lennard-Jones potential for its convenience and simplicity. The difficult task is to locate appropriate values of σ and ϵ. Some values are shown in Appendix B. Brokaw suggests other relations, e.g., Eq. (11-3.9) and (11-3.10). Even after the pure component values of σ and ϵ have been selected, a combination rule is necessary to obtain σ_{AB} and ϵ_{AB}. Most studies have employed Eqs. (11-3.4) and (11-3.5) because they are simple and theory suggests no particularly better alternatives. Ravindran et al. [174] have used Eq. (11-3.2) to correlate diffusivities of low-volatile organics in light gases.

It is important to employ values of σ and ϵ obtained from the same source. Published values of these parameters differ considerably, but σ and ϵ from a single source often lead to the same result as the use of a quite different pair from another source.

The estimation equations described in this section were used to calculate diffusion coefficients for a number of different gases, and the results are shown in Table 11-2. The accuracy of the theoretical relations is discussed in Sec. 11-4 after some empirical correlations for the diffusion coefficient have been described.

11-4   Diffusion Coefficients for Binary Gas Systems at Low Pressures: Empirical Correlations

Several proposed methods for estimating D_{AB} in low-pressure binary gas systems retain the general form of Eq. (11-3.2), with empirical constants based on experimental data. These include the equations proposed by Arnold [11], Gilliland [77], Wilke and Lee [231], Slattery and Bird [193], Bailey [14], Chen and Othmer [38], Othmer and Chen [163], and Fuller

et al. [68, 69, 70]. Values of D_{AB} estimated by these equations generally agree with experimental values to within 5 to 10 percent, although discrepancies of more than 20 percent are possible. We illustrate two methods which have been shown to be quite general and reliable.

Wilke and Lee [231]

Equation (11-3.2) is rewritten as

$$D_{AB} = \frac{[3.03 - (0.98/M_{AB}^{1/2})](10^{-3})T^{3/2}}{PM_{AB}^{1/2}\sigma_{AB}^2\Omega_D} \tag{11-4.1}$$

where D_{AB} = binary diffusion coefficient, cm^2/s
$\quad\quad T$ = temperature, K
M_A, M_B = molecular weights of A and B, g/mol
$\quad M_{AB} = 2[(1/M_A) + (1/M_B)]^{-1}$
$\quad\quad P$ = pressure, bar

The scale parameter σ_{AB} is given by Eq. (11-3.5) where, for each component,

$$\sigma = 1.18V_b^{1/3} \tag{11-4.2}$$

and V_b is the liquid molar volume, cm^3/mol, found from experimental data or estimated from the Le Bas contributions in Table 3-8. Ω_D is determined from Eq. (11-3.6) with $(\epsilon/k)_{AB}$ from Eq. (11-3.4) and, for each component,

$$\frac{\epsilon}{k} = 1.15T_b \tag{11-4.3}$$

with T_b as the normal boiling point (at 1 atm) in kelvins. Note, for systems in which one component is air, σ (air) = 3.62 Å and ϵ/k (air) = 97.0 K. We illustrate this method in Example 11-3.

Fuller et al. [68, 69, 70]

These authors modified Eq. (11-3.2) to

$$D_{AB} = \frac{0.00143\,T^{1.75}}{PM_{AB}^{1/2}[(\Sigma_v)_A^{1/3} + (\Sigma_v)_B^{1/3}]^2} \tag{11-4.4}$$

where the terms have been defined under Eq. (11-4.1) and Σ_v is found for each component by summing atomic diffusion volumes in Table 11-1 [69]. These atomic parameters were determined by a regression analysis of many experimental data, and the authors report an average absolute error

TABLE 11-1   Atomic Diffusion Volumes

Atomic and Structural Diffusion Volume Increments			
C	15.9	F	14.7
H	2.31	Cl	21.0
O	6.11	Br	21.9
N	4.54	I	29.8
Aromatic ring	−18.3	S	22.9
Heterocyclic ring	−18.3		

Diffusion Volumes of Simple Molecules			
He	2.67	CO	18.0
Ne	5.98	CO_2	26.9
Ar	16.2	N_2O	35.9
Kr	24.5	NH_3	20.7
Xe	32.7	H_2O	13.1
H_2	6.12	SF_6	71.3
D_2	6.84	Cl_2	38.4
N_2	18.5	Br_2	69.0
O_2	16.3	SO_2	41.8
Air	19.7		

of about 4 percent when using Eq. (11-4.4). The technique is illustrated in Example 11-3.

Discussion

In Table 11-2 we show experimental diffusion coefficients for a number of binary systems and note the errors found when estimating D_{AB} for (a) the basic theoretical equation (11-3.2), (b) Brokaw's method [Eqs. (11-3.2) and (11-3.7)], (c) Wilke and Lee's method [Eq. (11-4.1)], and (d) Fuller et al.'s method [Eq. (11-4.4)]. For (a), no calculations were made if σ and ϵ/k were not available in Appendix B.

For all methods, there were always a few systems for which large errors were found. These differences may be due to inadequacies of the method or to inaccurate data. In general, however, the Fuller et al. procedure [Eq. (11-4.4) and Table 11-1] yielded the smallest average error, and it is the method recommended for use. Other evaluations [60, 81, 82, 129, 166] have shown both the Fuller et al. and the Wilke-Lee forms to be reliable. The results found when using the Brokaw method were erratic; also, no special advantage was demonstrated for this method when applied to mixtures containing polar components.

A review of experimental data of binary diffusion coefficients is available [80].

Example 11-3 Estimate the diffusion coefficient of allyl chloride (AC) in air at 298 K and 1 bar. The experimental value reported by Lugg [129] is 0.098 cm²/s.

solution WILKE AND LEE METHOD. As suggested in the text, for air $\sigma = 3.62$ Å and $\epsilon/k = 97.0$ K. For allyl chloride, from Appendix A, $T_b = 318.3$ K and, with Table 3-8, $V_b = (3)(14.8) + (5)(3.7) + 24.6 = 87.5$ cm^3/mol. Thus, using Eqs. (11-4.2) and (11-4.3),

$$\sigma \, (AC) = (1.18)(87.5)^{1/3} = 5.24 \text{ Å}$$
$$\epsilon \, (AC)/k = (1.15)(318.3) = 366 \text{ K}$$

Then, with Eqs. (11-3.4) and (11-3.5)

$$\epsilon \, (AC\text{-air})k = [(366)(97.0)]^{1/2} = 188 \text{ K}$$
$$\sigma \, (AC\text{-air}) = (5.24 + 3.62)/2 = 4.43 \text{ Å}$$
$$T^* = \frac{T}{\epsilon \, (AC\text{-air})k} = \frac{298}{188} = 1.59$$

and, with Eq. (11-3.6), $\Omega_D = 1.17$. With M (AC) $= 76.5$ and M (air) $= 29.0$, $M_{AB} = (2)[(1/76.5) + (1/29.0)]^{-1} = 42.0$. Finally, with Eq. (11-4.1) when $P = 1$ bar,

$$D = \frac{\{3.03 - [0.98/(42.0)^{1/2}]\}(10^{-3})(298)^{3/2}}{(1)(42.0)^{1/2}(4.43)^2(1.17)}$$

$$= 0.10 \text{ cm}^2/\text{s}$$

$$\text{Error} = \frac{0.10 - 0.098}{0.098} \times 100 = 2\%$$

FULLER ET AL. METHOD. Equation (11-4.4) is used. $P = 1$ bar; M_{AB} was shown above to be equal to 42.0; and $T = 298$ K. For air $(\Sigma_v) = 19.7$, and for allyl chloride, C$_3$H$_5$Cl, with Table 11-1, $(\Sigma_v) = (3)(15.9) + (5)(2.31) + 21 = 80.25$. Thus,

$$D = \frac{(0.00143)(298)^{1.75}}{(1)(42.0)^{1/2}[(19.7)^{1/3} + (80.25)^{1/3}]^2}$$

$$= 0.096 \text{ cm}^2/\text{s}$$

$$\text{Error} = \frac{0.096 - 0.098}{0.098} \times 100 = -2\%$$

11-5 The Effect of Pressure on the Binary Diffusion Coefficients of Gases

At low to moderate pressures, binary diffusion coefficients vary inversely with pressure or density as suggested by Eqs. (11-3.1) and (11-3.2). At high pressures, the product DP or $D\rho$ is no longer constant but decreases with an increase in either P or ρ. Note that it is possible to have a different behavior in the products DP and $D\rho$ as the pressure is raised, since ρ is proportional to pressure only at low pressures, and gas nonidealities—with their concomitant effect on the system density—may become important. Also, as indicated earlier, at low pressures, the binary diffusion coefficient is essentially independent of composition. At high pressures, where the gas phase may deviate significantly from an ideal gas, small, but finite effects of composition have been noted, e.g., ref. 201.

TABLE 11-2 Comparison of Methods for Estimating Gas Diffusion Coefficients at Low Pressures

System	T, K	$D_{AB}P$ (obs.), (cm²/s) bar	Ref.	Errors as percent of observed values			
				Theoretical	Brokaw	Wilke-Lee	Fuller et al.
Air–carbon dioxide	276	0.144	103	-6	-1	6	-4
	317	0.179		-3	2	10	-2
Air–ethanol	313	0.147	139	-10	-13	-8	-9
Air–helium	276	0.632	103	0	-1	-2	-6
	346	0.914		0	0	-1	-3
Air–n-hexane	294	0.081	35	-6	-5	-4	-8
	328	0.094		-1	0	1	-4
Air–2-methylfuran	334	0.107	4	—	6	10	6
Air–naphthalene	303	0.087	28	—	-18	-17	-17
Air–water	313	0.292	35	-18	2	-9	-6
Ammonia–diethyl ether	288	0.101	197	-23	-13	-14	1
	337	0.139		-23	-13	-15	-3
Argon–ammonia	255	0.152	196	3	3	3	11
	333	0.256		3	2	1	5
Argon–benzene	323	0.085	134	8	9	14	13
	373	0.112		7	8	15	10
Argon–helium	276	0.655	103	-1	-6	-7	-3
	418	1.417	36	-10	-13	-15	-7
Argon–hexafluorobenzene	323	0.082	134	—	-7	-5	-18
	373	0.095		—	-5	-8	-10
Argon–hydrogen	295	0.84	229	-9	-2	-8	-5
	628	3.25		-15	-10	-16	-8
	1068	8.21		-19	-14	-20	-7
Argon–krypton	273	0.121	195	-1	-5	2	-2
Argon–methane	298	0.205	36	5	7	13	3
Argon–sulfur dioxide	263	0.078	139	24	17	23	22
Argon–xenon	195	0.052	36	-1	-3	5	7
	378	0.180		-2	-4	3	-1
Carbon dioxide–helium	298	0.620	188	-3	0	-2	-6
	498	1.433		-2	1	-1	0
Carbon dioxide–nitrogen	298	0.169	224	-9	-7	-1	-4
Carbon dioxide–nitrous oxide	313	0.130	6	-6	7	16	-3
Carbon dioxide–sulfur dioxide	473	0.198	139	8	10	16	13

System	T						
Carbon dioxide–tetrafluoromethane	298	0.087	112	-1	4	13	-12
	673	0.385		-4	4	12	-17
Carbon dioxide–water	307	0.201	41	-20	-5	-8	9
Carbon monoxide–nitrogen	373	0.322	5	-6	-6	0	-5
Ethylene–water	328	0.236	186	-7	-6	-10	-4
Helium–benzene	423	0.618	188	8	19	7	-6
Helium–bromobenzene	427	0.550	69	—	30	13	-3
Helium–2-chlorobutane	429	0.568	69	—	25	9	-3
Helium–n-butanol	423	0.595	188	10	3	7	-3
Helium–1-iodobutane	428	0.524	69	—	26	10	0
Helium–methanol	432	1.046	188	7	6	-2	-3
Helium–nitrogen	298	0.696	188	1	1	-1	1
Helium–water	352	1.136	186	1	20	-5	-1
Hydrogen–acetone	296	0.430	139	0	32	6	1
Hydrogen–ammonia	263	0.58	139	4	23	4	5
	358	1.11		-4	11	-6	-5
	473	1.89		-5	6	-12	-9
Hydrogen–cyclohexane	289	0.323	105	-3	31	10	-4
Hydrogen–naphthalene	303	0.305	28	—	32	8	3
Hydrogen–nitrobenzene	493	0.831	166	—	23	2	2
Hydrogen–nitrogen	294	0.773	187	-5	6	-2	-1
	573	2.449		-8	2	-5	0
Hydrogen–pyridine	318	0.443	105	-5	22	3	4
Hydrogen–water	307	0.927	41	-12	24	-2	3
Methane–water	352	0.361	186	-11	3	-3	-2
Nitrogen–ammonia	298	0.233	139	-5	-3	-4	-3
	358	0.332		-6	-3	-6	-6
Nitrogen–aniline	473	0.182	166	—	5	8	7
Nitrogen–sulfur dioxide	263	0.105	139	-3	-2	2	-1
Nitrogen–water	308	0.259	186	-11	4	-2	5
	352	0.364		-17	-3	-10	-1
Nitrogen–sulfur hexafluoride	378	0.146	112	—	6	11	-1
Oxygen–benzene	311	0.102	105	-9	-5	-2	-4
Oxygen–carbon tetrachloride	296	0.076	139	-5	1	3	-4
Oxygen–cyclohexane	289	0.076	105	-7	3	4	-2
Oxygen–water	352	0.357	186	-15	-1	-6	-1
Average absolute error				7.3	9.0	7.0	5.4

There are few experimental studies of binary diffusion coefficients at high pressures, and many of the more recent data involve a trace solute in a supercritical fluid [50, 67, 108, 151, 184, 199, 207, 220] or relate to systems containing helium as one component [13].

With the paucity of reliable data, it is not surprising that few estimation methods have been proposed. Takahashi [200] has suggested a very simple corresponding states method which is satisfactory for the limited data base available. His correlation is

$$\frac{D_{AB}P}{(D_{AB}P)^+} = f(T_r, P_r) \tag{11-5.1}$$

where D_{AB} = diffusion coefficient, cm^2/s
$\quad\quad P$ = pressure, bar

The superscript $^+$ indicates that low-pressure values are to be used. The function $f(T_r, P_r)$ is shown in Fig. 11-3, and to obtain pseudocritical properties from which to calculate the reduced temperatures and pressures, Eqs. (11-5.2) to (11-5.5) are used.

$$T_r = \frac{T}{T_c} \tag{11-5.2}$$

$$T_c = y_A T_{cA} + y_B T_{cB} \tag{11-5.3}$$

$$P_r = \frac{P}{P_c} \tag{11-5.4}$$

$$P_c = y_A P_{cA} + y_B P_{cB} \tag{11-5.5}$$
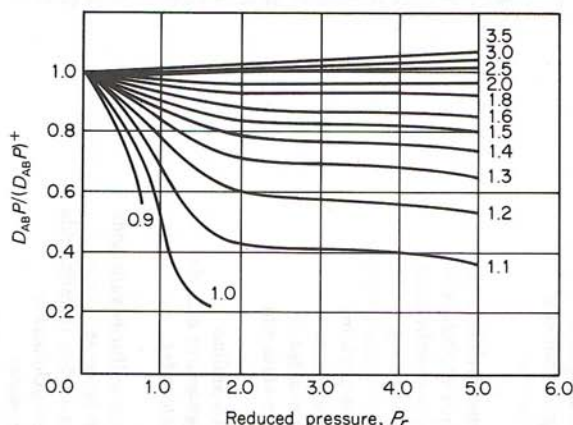
Figure 11-3 Takahashi correlation for the effect of pressure and temperature on the binary diffusion coefficient.

As an illustration of this technique, in Fig. 11-4, we have plotted the data of Takahashi and Hongo [201] for the system carbon dioxide–ethylene. Two cases are considered, one with a very low concentration of ethylene and the other with a very low concentration of carbon dioxide. Up to about 80 bar, the two limiting diffusion coefficients are essentially identical. Above that pressure, D_{AB} for the trace CO_2 system is significantly higher. Plotted as solid curves on this graph are the predicted values of D_{AB} from Fig. 11-3 using the $(D_{AB}P)^+$ product at low pressure to be 0.149 (cm^2/s)bar as found by Takahashi and Hongo. Also, the dashed curve has been drawn to indicate the estimated value of D_{AB} if one had assumed that $D_{AB}P$ was a constant. Clearly this assumption is in error above a pressure of about 10 to 15 bar.

Tee et al. [204] suggested a similar corresponding states approach, as have others [156, 189, 190, 201].
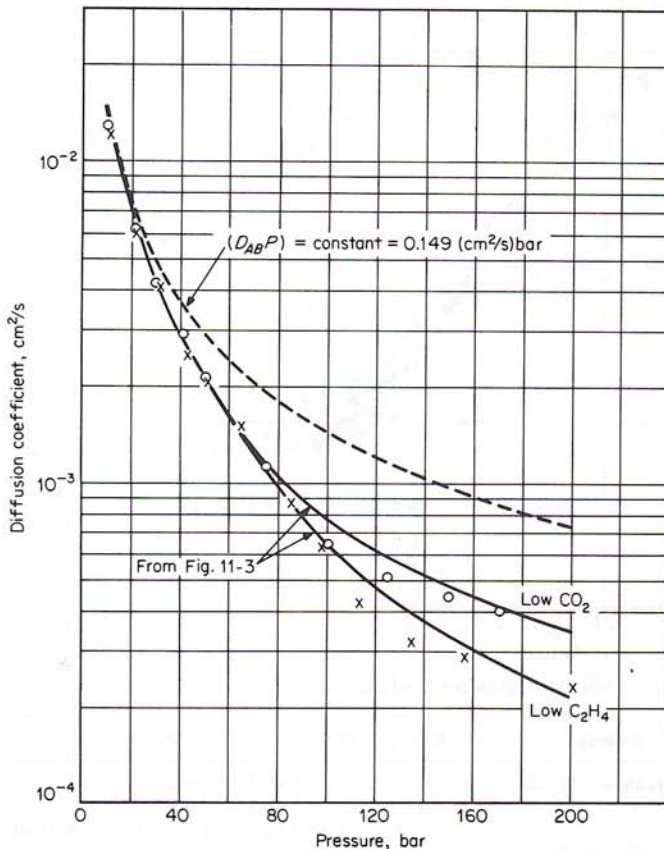
Figure 11-4 Effect of pressure and composition on the binary diffusion coefficient in the CO_2–C_2H_4 system.

To illustrate some data for the diffusion coefficient of complex solutes in supercritical fluids, we show Fig. 11-5. There the diffusion coefficient is given as a function of reduced pressure from the ideal-gas range to reduced pressures up to about 6. The solutes are relatively complex molecules, and the solvent gases are CO_2, ethylene, and SF_6. No temperature dependence is shown, since the temperatures studied (see legend) were such that all the reduced temperatures were similar and were, in most cases, in the range of 1 to 1.05.† Up to about half the critical pressure, $D_{AB}P$ is essentially constant. Above that pressure, the data show the product $D_{AB}P$ decreasing, and at reduced pressures of about 2, it would appear that $D_{AB} \propto P_r^{1/2}$. As supercritical extractions are often carried out in a reduced temperature range of about 1.1 to 1.2 and in a reduced pressure range of 2 to 4, this plot would indicate that $D_{AB} \simeq 10^{-4}$ cm²/s, a value much less than for a low-pressure gas but still significantly higher than

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†Since the concentrations of the solutes were quite low, the pressure and temperature were reduced by the pure component values of P_c and T_c of the solvents.
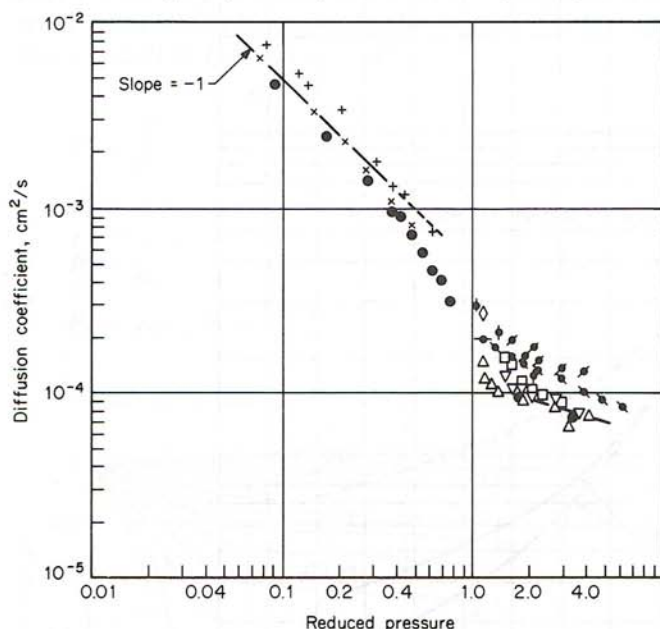
Figure 11-5   Diffusion coefficients in supercritical fluids.

Key	T, °C	System	Key	T, °C	System
●	20	CO_2-naphthalene [151, 220]	↑	40	CO_2-benzene [184]
×	30		●	40	CO_2-propylbenzene [199]
+	40		◇	40	CO_2-1,2,3-trimethylbenzene [199]
△	35	CO_2-naphthalene [108, 207]			
▽	55				SF_6-naphthalene [50]
↖	12	Ethylene-naphthalene [108, 207]		55	SF_6-benzoic acid [50]
↗	35				

for a typical liquid (see Sec. 11-9).
We illustrate Takahashi's correlation in Example 11-4.

Example 11-4 Estimate the diffusion coefficient of 2-naphthol in supercritical carbon dioxide at 318 K and 165 bar. The experimental value is reported to be about 7.4×10^{-5} cm²/s [50].

solution This estimation problem is typical of the problems often encountered. We have no knowledge of the low-pressure diffusion coefficient for this system, and, in fact, experimental values of the critical properties of 2-naphthol are unavailable. However, we suspect that the concentration of 2-naphthol is quite low, so that Takahashi's rules in Eqs. (11-5.2) to (11-5.5) would reduce to T_c and P_c for the pure solvent (CO_2). Since $T_c = 304.2$ K and $P_c = 73.8$ bar for CO_2, then $T_r = 318/304.2 = 1.05$ and $P_r = 165/73.8 = 2.24$. With Fig. 11-3,

$$\frac{D_{AB}P}{(D_{AB}P)^+} \approx 0.3$$

To estimate D_{AB}^+ (at 1 bar), we will use the Fuller et al. method from Sec. 11-4. For CO_2, $M = 44.01$ and $(\Sigma_v) = 26.9$ from Table 11-1. For 2-naphthol, $M = 144$ and $(\Sigma_v) = (10)(C) + (8)(H) + (1)(O) +$ aromatic ring $= (10)(15.9) + (8)(2.31) + (1)(6.11) - 18.3 = 165.2$. Then, with Eq. (11-4.4) and $P = 1$ bar, $T = 318$ K, $M_{AB} = 2[(1/44.01) + (1/144)]^{-1} = 67.4$,

$$D_{AB}^+ = \frac{(0.00143)(318)^{1.75}}{(1)(67.4)^{1/2}[(26.9)^{1/3} + (165.2)^{1/3}]^2} = 5.1 \times 10^{-2} \text{ cm}^2/\text{s}$$

$$D_{AB} = \frac{(0.30)(5.1 \times 10^{-2})}{165} = 9.2 \times 10^{-5} \text{ cm}^2/\text{s}$$

This result is about 25 percent higher than that reported experimentally. On the other hand, the estimated value falls well within the band of data in Fig. 11-5 at $P_r \simeq 2$.
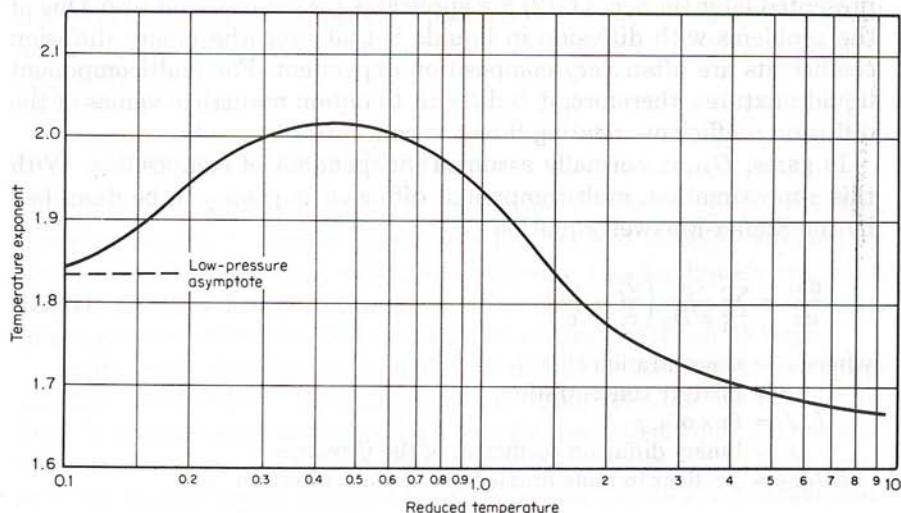
Figure 11-6 Exponent of temperature for diffusion in gases. (*Adapted from Ref. 138 with the approximation that $\epsilon/k \approx 0.75 T_c$.*)

11-6   The Effect of Temperature on Diffusion in Gases

At low pressures, where the ideal-gas law approximation is valid, it is seen from Eq. (11-3.2) that

$$D_{AB} \propto \frac{T^{3/2}}{\Omega_D(T)} \tag{11-6.1}$$

or $$\left(\frac{\partial \ln D_{AB}}{\partial \ln T}\right)_P = \frac{3}{2} - \frac{d \ln \Omega_D}{d \ln T} \tag{11-6.2}$$

Marrero and Mason [138] indicate that, in most cases, the term $d \ln \Omega_D/d \ln T$ varies from 0 to $-\frac{1}{2}$. Thus D_{AB} varies as $T^{3/2}$ to T^2. This result agrees with the empirical estimation methods referred to in Sec. 11-4, e.g., in the Fuller et al. method, $D \propto T^{1.75}$. Over wide temperature ranges, however, the exponent on temperature changes. Figure 11-6 shows the approximate variation of this exponent with reduced temperature. The very fact that the temperature exponent increases and then decreases indicates that empirical estimation techniques with a constant exponent will be limited in their range of applicability. The theoretical and the Wilke-Lee methods are therefore preferable if wide temperature regions are to be covered.

11-7   Diffusion in Multicomponent Gas Mixtures

A few general concepts of diffusion in multicomponent liquid mixtures presented later (in Sec. 11-12) are applicable for gas mixtures also. One of the problems with diffusion in liquids is that even the binary diffusion coefficients are often very composition-dependent. For multicomponent liquid mixtures, therefore, it is difficult to obtain numerical values of the diffusion coefficients relating fluxes to concentration gradients.

In gases, D_{AB} is normally assumed independent of composition. With this approximation, multicomponent diffusion in gases can be described by the Stefan-Maxwell equation

$$\frac{dx_i}{dz} = \sum_{j=1}^{n} \frac{c_i c_j}{c^2 D_{ij}} \left(\frac{J_j}{c_j} - \frac{J_i}{c_i}\right) \tag{11-7.1}$$

where c_i = concentration of i
c = mixture concentration.
J_i, J_j = flux of i, j
D_{ij} = binary diffusion coefficient of the ij system
(dx_i/dz) = gradient in mole fraction of i in the z direction

This relation is different from the basic binary diffusion relation (11-

2.5), but the employment of common binary diffusion coefficients is particularly desirable. Marrero and Mason [138] discuss many of the assumptions behind Eq. (11-7.1).

Few attempts have been made by engineers to calculate fluxes in multicomponent systems. However, one important and simple limiting case is often cited. If a dilute component i diffuses into a *homogeneous* mixture, then $J_j \approx 0$. With $c_j/c = x_j$, Eq. (11-7.1) reduces to

$$\frac{dx_i}{dz} = -J_i \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{x_j}{cD_{ij}} \tag{11-7.2}$$

Defining

$$D_{i_m} = \frac{-J_i}{dx_i/dz} \tag{11-7.3}$$

gives

$$D_{i_m} = \left(\sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{x_j}{D_{ij}} \right)^{-1} \tag{11-7.4}$$

This simple relation (sometimes called Blanc's law [21, 138]) was shown to apply to several ternary cases in which i was a trace component [140]. Deviations from Blanc's law are discussed by Sandler and Mason [181].

The general theory of diffusion in multicomponent gas systems is covered by Cussler [47] and by Hirschfelder et al. [100]. The problem of diffusion in three-component gas systems has been generalized by Toor [206] and verified by Fairbanks and Wilke [64], Walker et al. [223], and Duncan and Toor [56].

11-8   Diffusion in Liquids: Theory

Binary liquid diffusion coefficients are defined by Eq. (11-2.5) or (11-2.7). Since molecules in liquids are densely packed and strongly affected by force fields of neighboring molecules, values of D_{AB} for liquids are much smaller than for low-pressure gases. That does not mean that diffusion rates are necessarily low, since concentration gradients can be large.

Liquid state theories for calculating diffusion coefficients are quite idealized, and none is satisfactory in providing relations for calculating D_{AB}. In several cases, however, the *form* of a theoretical equation has provided the framework for several useful prediction methods. A case in point involves the analysis of large spherical molecules diffusing in a dilute solution. Hydrodynamic theory [20, 73] then indicates that

$$D_{AB} = \frac{RT}{6\pi\eta_B r_A} \qquad (11\text{-}8.1)$$

where η_B is the viscosity of the solvent and r_A is the radius of the "spherical" solute. Equation (11-8.1) is the Stokes-Einstein equation. Although this fixed relation was derived for a very special situation, many authors have used the form as a starting point in developing correlations.

Other theories for modeling diffusion in liquids have been based on kinetic theory [10, 18, 31, 33, 48, 52, 91, 114, 148], absolute-rate theory [45, 62, 73, 78, 124, 127, 161, 176], statistical mechanics [17, 18, 111], and other concepts [3, 24, 104, 119, 120, 169]. Several reviews are available for further consideration [53, 75, 76, 99, 128].

Diffusion in liquid metals is not treated, although estimation techniques are available [165].

11-9 Estimation of Binary Liquid Diffusion Coefficients at Infinite Dilution

For a binary mixture of solute A in solvent B, the diffusion coefficient D_{AB}° of A diffusing in an infinitely dilute solution of A in B implies that each A molecule is in an environment of essentially pure B. In engineering work, however, D_{AB}° is assumed to be a representative diffusion coefficient even for concentrations of A up to 5 and perhaps 10 mole percent.

In this section, several estimation methods for D_{AB}° are introduced; the effect of concentration for mutual diffusion coefficients is covered in Sec. 11-10.

Wilke-Chang estimation method [230]

An older but still widely used correlation for D_{AB}°, the Wilke-Chang technique is, in essence, an empirical modification of the Stokes-Einstein relation (11-8.1):

$$D_{AB}^\circ = \frac{7.4 \times 10^{-8}(\phi M_B)^{1/2}T}{\eta_B V_A^{0.6}} \qquad (11\text{-}9.1)$$

where D_{AB}° = mutual diffusion coefficient of solute A at very low concentrations in solvent B, cm^2/s

M_B = molecular weight of *solvent* B, g/mol

T = temperature, K

η_B = viscosity of *solvent* B, cP

V_A = molar volume of *solute* A at its normal boiling temperature, cm^3/mol

ϕ = *association factor* of solvent B, dimensionless

If experimental data to obtain V_A at T_b do not exist, estimation methods from Chap. 3 may be used, in particular the Le Bas additive volume table (3-8) is convenient.

Wilke and Chang recommend that ϕ be chosen as 2.6 if the solvent is water, 1.9 if it is methanol, 1.5 if it is ethanol, and 1.0 if it is unassociated. When 251 solute-solvent systems were tested by these authors, an average error of about 10 percent was noted. Figure 11-7 is a graphical representation of Eq. (11-9.1) with the dashed line representing Eq. (11-8.1); the latter is assumed to represent the maximum value of the ordinate for any value of V_A.

A number of authors have suggested modifications of Eq. (11-9.1) particularly to improve its accuracy for systems where water is the solute and the solvent is an organic liquid [7, 29, 93, 94, 97, 123, 130, 133, 160, 183, 191, 232, 233]. However, none of these suggestions have been widely accepted. In Table 11-5, we show a comparison of estimated and experimental values of D_{AB}°. The errors vary so greatly that the concept of an *average* error is meaningless. The method should not be used when water is the *solute*.

Example 11-5 Use the Wilke-Chang correlation to estimate D_{AB}° for ethylbenzene diffusing into water at 293 K. The viscosity of water at this temperature is essentially 1.0 cP. The experimental value of D_{AB}° is 0.81×10^{-5} cm^2/s [233].

solution The normal boiling point of ethylbenzene is 409.3 K (Appendix A). At that temperature, the density is 0.761 g/cm^3 [217], so with $M_A = 106.17$, $V_A = 106.17/0.761 = 139.5$ cm^3/mol. [If Table 3-8 has been used, $V_A = (14.8)(8) + (3.7)(10) - 15 = 140$ cm^3/mol.] Then, using Eq. (11-9.1) with $\phi = 2.6$ and $M_B = 18.0$ for water,
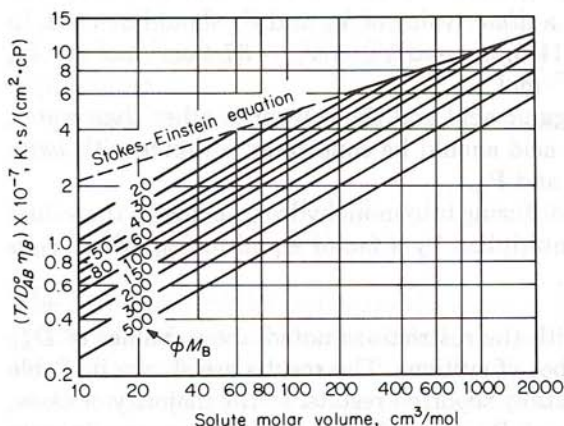
Figure 11-7 Graphical representation of Wilke-Chang correlation of diffusion coefficients in dilute solutions. *(From Ref. 230.)*

$$D_{AB}^\circ = 7.4 \times 10^{-8} \frac{[(2.6)(18.0)]^{1/2}(293)}{(1.0)(139.5)^{0.6}} = 0.77 \times 10^{-5} \text{ cm}^2/\text{s}$$

$$\text{Error} = \frac{0.77 - 0.81}{0.81} \times 100 = -5\%$$

Tyn and Calus method [212]

These authors have proposed that D_{AB}° be estimated by the relation

$$D_{AB}^\circ = 8.93 \times 10^{-8} \left(\frac{V_A}{V_B^2}\right)^{1/6} \left(\frac{P_B}{P_A}\right)^{0.6} \frac{T}{\eta_B} \tag{11-9.2}$$

where V_B = molar volume of the *solvent* at the normal boiling temperature, cm^3/mol, P_A and P_B are parachors for the solute and solvent, and the other terms are defined under Eq. (11-9.1).

The parachor is related to the liquid surface tension (see Chap. 12) as

$$P = V\sigma^{1/4} \tag{11-9.3}$$

where σ is the surface tension in $\text{dyn/cm} = \text{g/s}^2 = 10^{-3} \text{ N/m}^2$ and V is the molar volume, cm^3/mol, both measured at the same temperature. Thus the units of P are $\text{cm}^3 \cdot \text{g}^{1/4}/\text{s}^{1/2} \cdot \text{mol}$. Quayle [168] has tabulated values of P for a large number of chemicals; alternatively, P may be estimated from additive group contributions as shown in Table 11-3. Over moderate temperature ranges, P is essentially a constant.

When using the correlation shown in Eq. (11-9.2), the authors note several restrictions:

1. The method should *not* be used for diffusion in viscous solvents. Values of η_B above about 20 to 30 cP would classify the solvent as viscous.

2. If the solute is water, a *dimer* value of V_A and P_A should be used. In the calculations for Table 11-5, we used $V_A = V_w = 37.4 \text{ cm}^3/\text{mol}$ and $P_A = P_w = 105.2 \text{ cm}^3 \cdot \text{g}^{1/4}/\text{s}^{1/2} \cdot \text{mol}$.

3. If the solute is an organic acid and the solvent is other than water, methanol, or butanol, the acid should be considered a *dimer* with twice the expected values of V_A and P_A.

4. For nonpolar solutes diffusing into monohydroxy alcohols, the values of V_B and P_B should be multiplied by a factor equal to $8\eta_B$, where η_B is the solvent viscosity in cP.

By using Eq. (11-9.2) with the restrictions noted above, values of D_{AB}° were estimated for a number of systems. The results are shown in Table 11-5, along with experimentally reported results. In the majority of cases, quite reasonable estimates of D_{AB}° were found and errors normally were less than 10%.

TABLE 11-3 Structural Contributions for Calculating the Parachor†

Carbon-hydrogen:		R−[−CO−]−R′ (ketone)	
C	9.0	R + R′ = 2	51.3
H	15.5	R + R′ = 3	49.0
CH₃	55.5	R + R′ = 4	47.5
CH₂ in −(CH₂)ₙ		R + R′ = 5	46.3
$n < 12$	40.0	R + R′ = 6	45.3
$n > 12$	40.3	R + R′ = 7	44.1
		−CHO	66
Alkyl groups		O (not noted above)	20
1-Methylethyl	133.3	N (not noted above)	17.5
1-Methylpropyl	171.9	S	49.1
1-Methylbutyl	211.7	P	40.5
2-Methylpropyl	173.3	F	26.1
1-Ethylpropyl	209.5	Cl	55.2
1,1-Dimethylethyl	170.4	Br	68.0
1,1-Dimethylpropyl	207.5	I	90.3
1,2-Dimethylpropyl	207.9		
1,1,2-Trimethylpropyl	243.5	Ethylenic bonds:	
C₆H₅	189.6	Terminal	19.1
		2,3-position	17.7
Special groups:		3,4-position	16.3
−COO−	63.8		
−COOH	73.8	Triple bond	40.6
−OH	29.8		
−NH₂	42.5	Ring closure:	
−O−	20.0	Three-membered	12
−NO₂	74	Four-membered	6.0
−NO₃ (nitrate)	93	Five-membered	3.0
−CO(NH₂)	91.7	Six-membered	0.8

†As modified from Ref. 168.

To use the Tyn-Calus form, however, the parachors of both the solute and the solvent must be known. Although the compilation of Quayle [168] is of value, it is still incomplete. The structural contributions given in Table 11-3 also are incomplete, and many functional groups are not represented.

A modified form of Eq. (11-9.2) may be developed by combining Eqs. (11-9.2) and (11-9.3) to give

$$D_{AB}^{\circ} = 8.93 \times 10^{-8} \frac{V_B^{0.267}}{V_A^{0.433}} \frac{T}{\eta_B} \left(\frac{\sigma_B}{\sigma_A} \right)^{0.15} \tag{11-9.4}$$

The definitions of the terms are the same as before except, when substituting Eq. (11-9.3), we must define V and σ at T_b. Thus σ_B and σ_A in Eq. (11-9.4) refer to surface tensions at T_b. Note also the very low exponent on this ratio of surface tensions. Since most *organic* liquids at T_b have similar surface tensions, one might choose to approximate this ratio as equal to unity. (For example, $0.8^{0.15} = 0.97$ and $1.2^{0.15} = 1.03$.) Then,

$$D_{AB}^{\circ} = 8.93 \times 10^{-8} \frac{V_B^{0.267}}{V_A^{0.433}} \frac{T}{\eta_B} \tag{11-9.5}$$

Alternatively, an approximation to the σ_B/σ_A ratio may be developed by using one of the correlations shown in Chap. 12. For example, if the Brock and Bird corresponding states method were used, then

$$\sigma = P_c^{2/3} T_c^{1/3}(0.132\alpha_c - 0.278)(1 - T_{b_r})^{11/9} \tag{11-9.6}$$

with P_c in bars and T_b and T_c in kelvins, $T_{b_r} = T_b/T_c$, and

$$\alpha_c = 0.9076\left[1 + \frac{T_{b_r} \ln (P_c/1.013)}{1 - T_{b_r}}\right] \tag{11-9.7}$$

Equation (11-9.6) is only approximate, but it may be satisfactory when used to develop the *ratio* (σ_A/σ_B). Also, considering the low power (0.15) to which the ratio is raised, estimates of $(\sigma_B/\sigma_A)^{0.15}$ should be quite reasonable.

When Eq. (11-9.5) was employed to estimate D_{AB}° for the systems shown in Table 11-5, the results, as expected, were very similar to those found from the original Tyn and Calus form [Eq. (11-9.2)] except when σ_B differed appreciably from σ_A, for example, in the case of water and an organic liquid. In such situations, however, Eq. (11-9.4) with Eqs. (11-9.6) and (11-9.7) still led to results not significantly different from those with Eq. (11-9.2).

The various forms of the Tyn-Calus correlation are illustrated in Example 11-6.

Hayduk and Minhas correlation [98]

These authors considered many correlations for the infinite dilution binary diffusion coefficient. By regression analysis, they proposed several depending on the type of solute-solvent system.

For *normal paraffin solutions:*

$$D_{AB}^{\circ} = 13.3 \times 10^{-8} \frac{T^{1.47} \eta_B^{\epsilon}}{V_A^{0.71}} \tag{11-9.8}$$

where $\epsilon = (10.2/V_A) - 0.791$ and the other notation is the same as in Eq. (11-9.1). Equation (11-9.8) was developed from data on solutes ranging from C_5 to C_{32} in normal paraffin solvents encompassing C_5 to C_{16}. An average error of only 3.4 percent was reported.

For *solutes in aqueous solutions:*

$$D_{AB}^{\circ} = 1.25 \times 10^{-8}(V_A^{-0.19} - 0.292) T^{1.52} \eta_w^{\epsilon^*} \tag{11-9.9}$$

with $\epsilon^* = (9.58/V_A) - 1.12$. The rest of the terms are defined in the same

manner as under Eq. (11-9.1) except that the subscript w refers to the solvent, water. The authors report that this relation predicted D°_{AB} values with an average deviation of slightly less than 10 percent.

For *nonaqueous (nonelectrolyte) solutions:*

$$D^\circ_{AB} = 1.55 \times 10^{-8} \frac{T^{1.29}(\mathbf{P}^{0.5}_B/\mathbf{P}^{0.42}_A)}{\eta^{0.92}_B V^{0.23}_B} \tag{11-9.10}$$

The notation is the same as in Eq. (11-9.2).

The appropriate equation in the set of (11-9.8) to (11-9.10) was used in computing the errors shown in Table 11-5.

It is important to note that, when using the Hayduk-Minhas correlations, the same restrictions apply as in the Tyn-Calus equations.

If Eq. (11-9.3) is used in Eq. (11-9.10) to eliminate the parachors, one obtains

$$D^\circ_{AB} = 1.55 \times 10^{-8} \frac{V^{0.27}_B}{V^{0.42}_A} \frac{T^{1.29}}{\eta^{0.92}_B} \frac{\sigma^{0.125}_B}{\sigma^{0.105}_A} \tag{11-9.11}$$

This relation is remarkably similar to the modified Tyn-Calus equation (11-9.4) except for the larger exponent on temperature. As before, when σ_A and σ_B are not greatly different, the surface tension ratio may be set equal to unity as was done to obtain Eq. (11-9.5), or if σ_A and σ_B differ appreciably, Eqs. (11-9.6) and (11-9.7) may be employed.

Example 11-6 Estimate the infinitely dilute diffusion coefficient of acetic acid into acetone at 313 K. The experimental value is 4.04×10^{-5} cm²/s [230].

solution The data, from Appendix A and Refs. 168 and 217, are:

	Acetic acid (solute) A	Acetone (solvent) B
T_b, K	391.1	329.2
T_c, K	592.7	508.1
P_c, bar	57.9	47.0
ρ (at T_b), g/cm³	0.939	0.749
M, g/mol	60.05	58.08
V (at T_b), cm³/mol	64.0	77.5
$\mathbf{P}$, cm·g$^{1/4}$/s$^{1/2}$·mol	129	162
η_B, cP		0.270

TYN-CALUS, Eq. (11-9.2). By rule 3, acetic acid should be treated as a dimer; thus, $V = (2)(64.0) = 128$ cm³/mol and $\mathbf{P} = (2)(129) = 258$ cm³·g$^{1/4}$/s$^{1/2}$·mol.

$$D^\circ_{AB} = 8.93 \times 10^{-8} \left(\frac{128}{(77.5)^2}\right)^{1/6} \left(\frac{162}{258}\right)^{0.6} \frac{313}{0.270}$$

$$= 4.12 \times 10^{-5} \text{ cm}^2/\text{s}$$

$$\text{Error} = \frac{4.12 - 4.04}{4.04} \times 100 = 2\%$$

MODIFIED TYN-CALUS, Eq. (11-9.5)

$$D_{AB}^\circ = 8.93 \times 10^{-8} \frac{(77.5)^{0.267}}{(128)^{0.433}} \frac{313}{0.270}$$

$$= 4.04 \times 10^{-5} \text{ cm}^2/\text{s}$$

Error = 0%

MODIFIED TYN-CALUS, Eqs. (11-9.4), (11-9.6), and (11-9.7).   For acetic acid, T_{b_r} = 391.1/592.7 = 0.660. With Eq. (11-9.7),

$$\alpha_c = 0.9076 \left\{ 1 + (0.660) \left[\frac{\ln (57.9/1.013)}{1 - 0.660} \right] \right\} = 8.031$$

Similarly, α_c for acetone = 7.316. Then, with Eq. (11-9.6),

$$\sigma_A = (57.9)^{2/3}(592.7)^{1/3}[(0.132)(8.031) - 0.278](1 - 0.660)^{11/9}$$

$$= 26.0 \text{ erg/cm}^2$$

For acetone, $\sigma_B = 19.9 \text{ erg/cm}^2$ and $(\sigma_B/\sigma_A)^{0.15} = 0.961$; thus,

$$D_{AB}^\circ = (4.04 \times 10^{-5})(0.961)$$

$$= 3.88 \times 10^{-5} \text{ cm}^2/\text{s}$$

$$\text{Error} = \frac{3.88 - 4.04}{4.04} \times 100 = -4\%$$

In this particular case, the use of the $(\sigma_B/\sigma_A)^{0.15}$ factor actually increased the error; in most other cases, however, errors were less when it was employed.

HAYDUK-MINHAS, Eq. (11-9.10)

$$D_{AB}^\circ = 1.55 \times 10^{-8}(313)^{1.29} \frac{(162)^{0.5}/(258)^{0.42}}{(0.270)^{0.92}(77.5)^{0.23}}$$

$$= 3.89 \times 10^{-5} \text{ cm}^2/\text{s}$$

$$\text{Error} = \frac{3.89 - 4.04}{4.04} \times 100 = -4\%$$

Nakanishi correlation [157]

In this method, empirical parameters were introduced to account for specific interactions between the solvent and the (infinitely dilute) solute. As originally proposed, the scheme was applicable only at 298.2 K. We have scaled the equation assuming $D_{AB}^\circ \eta_B/T$ to be constant.

$$D_{AB}^\circ = \left[\frac{9.97 \times 10^{-8}}{(I_A V_A)^{1/3}} + \frac{2.40 \times 10^{-8} A_B S_B V_B}{I_A S_A V_A} \right] \frac{T}{\eta_B} \tag{11-9.12}$$

where D_{AB}° is the diffusion coefficient of solute A in solvent B at low concentrations, cm^2/s. V_A and V_B are the liquid molar volumes of A and B at the system temperature T, cm^3/mol, and the factors I_A, S_A, S_B, and A_B are given in Table 11-4. η_B is the solvent viscosity, in cP.

Should the solute (pure) not be a liquid at 298 K, it is recommended that the liquid molar volume at the boiling point be obtained either from data or from correlations in Chap. 3. Then,

$$V_A\ (298.2\ \text{K})\ =\ \beta V_A(T_b) \tag{11-9.13}$$

where $\beta = 0.894$ for compounds that are solid at 298 K and $\beta = 1.065$ for compounds that are normally gases at 298 K (and 1 bar). For example, if oxygen is the solute, then, at the normal boiling point of 90.2 K, the molar liquid volume is 27.9 cm^3/mol (Appendix A). With Eq. (11-9.13), $V_A = (1.065)(27.9) = 29.7$ cm^3/mol.

Values of D_{AB}° were estimated for a number of solute-solvent systems and the results were compared with experimental values in Table 11-5. In this tabulation, V_A for water was set equal to the dimer value of 37.4 cm^3/mol to obtain more reasonable results. The poorest estimates were obtained with dissolved gases and with solutes in the more viscous solvents such as n-butanol. The use of definite values of I_A to account for solute polarity may cause problems, since it is often difficult to decide whether a compound should be counted as polar ($I_A = 1.5$) or not ($I_A = 1.0$). It might be better to select an average $I_A \simeq 1.25$ if there is doubt about the molecular polarity.

Example 11-7 Estimate the value of D_{AB}° for CCl$_4$ diffusing into ethanol at 298 K. At this temperature, the viscosity of ethanol is 1.08 cP. The experimental value of D_{AB}° is 1.50×10^{-5} cm^2/s [133].

solution For this system with CCl$_4$ as solute A and ethanol as solvent B, from Table 11-4, $I_A = 1$, $S_A = 1$, $A_B = 2$, and $S_B = 1$. From Appendix A, the liquid densities of CCl$_4$ and ethanol at 298 K are 1.584 and 0.785 g/cm^3. With $M_A = 153.82$ and $M_B = 46.07$, $V_A = 153.82/1.584 = 97.1$ cm^3/mol and $V_B = 46.07/0.785 = 58.7$ cm^3/mol. Then, with Eq. (11-9.12),

TABLE 11-4   Nakanishi Parameter Values for Liquid Diffusion Coefficients

Compound(s)	As solutes (A)†		As solvents (B)	
	I_A	S_A	A_B	S_B
Water	2.8 (1.8)‡	1	2.8	1
Methanol	2.2 (1.5)	1	2.0	1
Ethanol	2.5 (1.5)	1	2.0	1
Other monohydric alcohols	1.5	1	1.8	1
Glycols, organic acids, and other associated compounds	2.0	1	2.0	1
Highly polar materials	1.5	1	1.0	1
Paraffins ($5 \le n \le 12$)	1.0	0.7	1.0	0.7
Other substances	1.0	1	1.0	1

†If the solute is He, H$_2$, D$_2$, or Ne, the values of V_A should be multiplied by $[1 + (0.85)\Lambda^2]$, where $\Lambda = 3.08$ for He^3, 2.67 for He^4, 1.73 for H$_2$, 1.22 for D$_2$, and 0.59 for Ne.

‡The values in parentheses are for cases in which these solutes are dissolved in a solvent which is more polar.

$$D_{AB}^{\circ} = \left[\frac{9.97 \times 10^{-8}}{(97.1)^{1/3}} + \frac{(2.40 \times 10^{-8})(2)(58.7)}{97.1} \right] \frac{298}{1.08}$$

$$= 1.40 \times 10^{-5} \text{ cm}^2/\text{s}$$

$$\text{Error} = \frac{1.40 - 1.50}{1.50} \times 100 = -7\%$$

Other infinite dilution correlations for diffusion coefficients have been proposed, but after evaluation they were judged either less accurate or less general than the ones noted above [1, 2, 3, 24, 39, 63, 65, 66, 71, 97, 116, 119, 120, 132, 164, 169, 175, 194, 205, 214, 215].

Effect of solvent viscosity

Most of the estimation techniques introduced in this section have assumed that D_{AB}° varies inversely with the viscosity of the solvent. This inverse dependence originated from the Stokes-Einstein relation for a large (spherical) molecule diffusing through a continuum solvent (small molecules). If, however, the solvent is viscous, one may question whether this simple relation is applicable. Davies et al. [49] found for CO_2 that in various solvents, $D_{AB}^{\circ}\eta_B^{0.45} \simeq$ constant for solvents ranging in viscosity from 1 to 27 cP, and these authors noted that, in 1930, Arnold [12] had proposed an empirical estimation scheme by which $D_{AB}^{\circ} \propto \eta_B^{-0.5}$. Oosting et al. [162] noted that, for the diffusion of 1-hexanol and 2-butanone in malto-dextrin solutions, the viscosity exponent was close to -0.5 over a range of temperatures and concentrations.

Hayduk and Cheng [95] investigated the effect of solvent viscosity more extensively and proposed that, for nonaqueous systems,

$$D_{AB}^{\circ} = Q\eta_B^q \tag{11-9.14}$$

where the constants Q and q are particular for a given solute; some values are listed by these authors. In Fig. 11-8, CO_2 diffusion coefficients in various solvents are shown. The solvent viscosity range is reasonably large, and the correlation for organic solvents is satisfactory. In contrast, the data for water as a solvent also are shown [99]. These data fall well below the organic solvent curve and have a slope close to -1. Hiss and Cussler [101] measured diffusion coefficients of n-hexane and naphthalene in hydrocarbons with viscosities ranging from 0.5 to 5000 cP and report that $D_{AB}^{\circ} \propto \eta_B^{-2/3}$, whereas Hayduk et al. [94] found that, for methane, ethane, and propane, D_{AB}° was proportional to $\eta_B^{-0.545}$.

These studies and others [73, 131, 225] show clearly that, over wide temperature or solvent viscosity ranges, simple empirical correlations, as presented earlier, are inadequate. The diffusion coefficient does not decrease in proportion to an increase in solvent viscosity, but $D_{AB}^{\circ} \propto \eta_B^q$, where q varies, usually from -0.5 to -1.
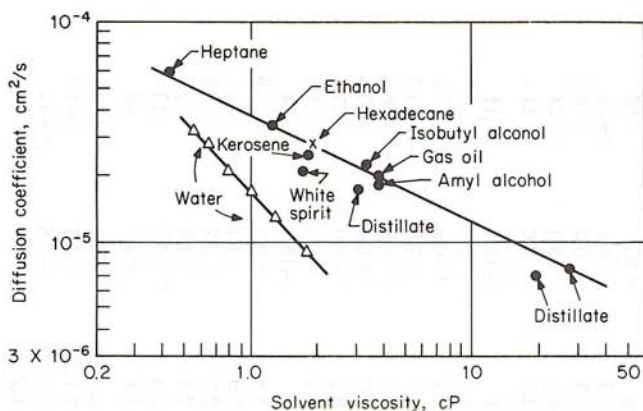
Figure 11-8 Diffusion coefficients of carbon dioxide in various solvents. ● Ref. 49; ✕ Ref. 95; △ Ref. 99

Discussion

Four estimation techniques were described to estimate the infinite dilution diffusion coefficient of a solute A in a solvent B. In Table 11-5, we show comparisons between calculated and experimental values of D_{AB}° for a number of binary systems. Several comments are pertinent when analyzing the results. First, the temperature range covered is small; thus, any conclusions based upon this sample may not hold at much higher (or lower) temperatures. Second, while D_{AB}° (exp.) is reported to three significant figures, the true accuracy is probably much less because diffusion coefficients are difficult to measure with high precision. Third, all estimation schemes tested showed wide fluctuations in the percent errors. These "failures" may be due to inadequacies in the correlation or to poor data. However, with such wide error ranges, the value of a single *average* percent error is in doubt and was not determined.

With these caveats, it is clearly seen that, in general, the Tyn-Calus and the Hayduk-Minhas correlations usually yield the lowest errors; they are, therefore, recommended for calculating D_{AB}°. Both require values of the solute and solvent parachors, but using modifications such as Eq. (11-9.5) when $\sigma_A \approx \sigma_B$, or Eq. (11-9.4) [or (11-9.10)] with, say, Eqs. (11-9.6) and (11-9.7) when σ_A differs much from σ_B obviates the necessity of knowing the parachors.

In special situations such as diffusion in n-paraffin solutions, Eq. (11-9.8) is recommended. We did not find a clear advantage for Eq. (11-9.9) over (11-9.2) for solutes diffusing into water, but the former would be more convenient to use.

New experimental data include the systems H_2S-H_2O [85], SO_2-H_2O [121], CO_2 in binary mixtures [202], normal paraffin solutions [96], hydrocarbons in n-hexane [57, 58], and rare gases in water [218]. Baldauf and

TABLE 11-5 Diffusion Coefficients in Liquids at Infinite Dilution

Solute A	Solvent B	T, K	$D^\circ_{AB} \times 10^5$, cm²/s	Ref.	Percent error†			
					Tyn and Calus	Hayduk and Minhas	Nakanishi	Wilke and Chang
Acetone	Chloroform	298	2.35	87	2.7	1.6	−7.6	39
		313	2.90		3.0	2.0	−7.3	39
Benzene		288	2.51	110	−22	−25	−14	0.4
		328	4.25	182	−24	−26	−16	−1.9
Ethanol		288	2.20	110	7.7	6.1	−25	53
Ethyl ether		298	2.13	182	1.9	0.3	8.3	27
Ethyl acetate		298	2.02	172	6.2	5.0	14	34
Methyl ethyl ketone		298	2.13	172	3.5	2.6	−11	34
Acetic acid	Benzene	298	2.09	37	−11	−11	−11	26
Aniline		298	1.96	170	1.4	1.5	−20	−3.1
Benzoic acid		298	1.38	37	−2.9	−0.8	−7.2	25
Bromobenzene		281	1.45	198	−8.5	−7.8	−4.3	−10
Cyclohexane		298	2.09	182	−8.5	−8.9	−6.0	−12
		333	3.45		−3.0	−3.9	−0.5	−7.0
Ethanol		288	2.25	110	−5.1	−6.0	−37	3.1
Formic acid		298	2.28	37	−5.7	−6.9	1.0	40
n-Heptane		298	2.10	30	−17	−18	−24	26
		353	4.25		−7.8	−9.4	6.5	26
Methyl ethyl ketone		303	2.09	7	7.9	7.1	−11	7.1
Naphthalene		281	1.19	198	2.7	3.7	3.2	−9.2
Toluene		298	1.85	182	2.4	2.0	5.5	−1.1
1,2,4-Trichlorobenzene		281	1.34	198	−7.3	−7.8	−13	−18
Vinyl chloride		281	1.77	198	−1.8	−2.1	19	5.6
Acetic acid	Acetone	288	2.92	19	6.3	−0.5	2.5	39
		313	4.04	230	2.1	−3.7	−1.6	33
Benzoic acid		298	2.62	37	−4.7	−7.8	−15	13
Formic acid		298	3.77	37	6.2	−0.6	17	56

Solvent	Solute						
	Nitrobenzene	293	2.94	175	8.5	3.6	−11	0.7
	Water	298	4.56	160	6.3	4.4	−16	—
n-Hexane	Bromobenzene	281	2.60	230	18	13	20	16
	Carbon tetrachloride	298	3.70	88	15	8.4	12	8.6
	Dodecane	298	2.73	215	9.2	−2.5	1.0	−13
	n-Hexane	298	4.21	135	−7.3	−2.6	2.2	−16
	Methyl ethyl ketone	303	3.74	7	24	19	−1.8	23
	Propane	298	4.87	94	2.4	22	13	6.0
	Toluene	298	4.21	37	−4.6	−9.1	−4.5	−6.9
Ethanol	Allyl alcohol	293	0.98	107	3.6	7.6	15	15
	Isoamyl alcohol	293	0.81	107	4.3	7.5	2.3	1.2
	Benzene	298	1.81	133	−1.5	3.6	−22	−40
	Iodine	298	1.32	37	—	—	−1.2	−1.5
	Oxygen	303	2.64	118	31	34	66	1.0
	Pyridine	293	1.10	107	−16	−14	−20	−17
	Water	298	1.24	123	3.4	12	7.5	−17
	Carbon tetrachloride	298	1.50	133	15	21	−6.7	−29
n-Butanol	Adipic acid	303	0.40	7	17	28	9.5	5.5
	Benzene	298	1.00	133	5.2	20	−21	−48
	Butyric acid	303	0.51	7	7.0	17	−5.6	6.8
	p-Dichlorobenzene	298	0.82	133	12	28	−27	−49
	Methanol	303	0.59	133	33	46	58	66
	Oleic acid	303	0.25	7	25	39	−13	1.1
	Propane	298	1.57	19	−23	−14	−39	−61
	Water	298	0.56	133	4.6	23	30	—
n-Heptane	Benzene	298	3.40	30	1.0	−1.6	12	7.4
		372	8.40		−3.0	−4.1	7.9	3.1
Ethyl acetate	Acetic acid	293	2.18	192	11	8.0	16	68
	Acetone	293	3.18	192	−7.2	−9.9	−14	2.5
	Ethyl benzoate	293	1.85	192	16	12	11	7.6
	Methyl ethyl ketone	303	2.93	7	3.9	1.1	−9.8	16
	Nitrobenzene	293	2.25	192	6.0	3.7	−11	9.3
	Water	298	3.20	123	11	13	−4.0	—

TABLE 11-5 Diffusion Coefficients in Liquids at Infinite Dilution (*Continued*)

Solute A	Solvent B	T, K	$D^{\circ}_{AB} \times 10^5$, cm^2/s	Ref.	Percent error†			
					Tyn and Calus	Hayduk and Minhas	Nakanishi	Wilke and Chang
Methane	Water	275	0.85	233	−1.6	1.0	22	10
		333	3.55		2.0	−2.5	27	15
Carbon dioxide		298	2.00	222	−19	−13	13	2.0
Propylene		298	1.44	222	−14	−11	1.1	−5.6
Methanol		288	1.26	110	−7.4	−4.0	−10	7.1
Ethanol		288	1.00	107	0	1.8	−7.7	11
Allyl alcohol		288	0.90	107	2.0	−0.2	−10	6.7
Acetic acid		293	1.19	126	−3.3	−4.6	−27	2.5
Ethyl acetate		293	1.00	126	−7.8	−15	−3.5	−10
Aniline		293	0.92	126	−4.0	−10	−18	−4.3
Diethylamine		293	0.97	126	−5.9	−14	−22	−10
Pyridine		288	0.58	107	44	22	14	33
Ethylbenzene		293	0.81	233	0.8	−14	1.9	−6.2
Methylcylopentane		275	0.48	233	2.1	−13	6.3	0
		293	0.85		2.5	−7.5	6.8	0
		333	1.92		10	9.7	15	7.3
Vinyl chloride		298	1.34	97	−5.8	−3.6	10	3.0
		348	3.67		−5.5	2.5	10	3.5

†Percent error = [(calc. − exp.)/exp.] × 100

Knapp [15] studied a wide variety of polar and nonpolar systems at different temperatures and compositions. Mohan and Srinivasan [150] discuss the effect of solute-solvent complexes on D_{AB}° for solutions of nonpolar solvents (benzene, carbon tetrachloride) with small amounts of methanol or ethanol.

11-10 Concentration Dependence of Binary Liquid Diffusion Coefficients

In Sec. 11-2 it was suggested that the diffusion coefficient D_{AB} in a binary mixture may be proportional to a thermodynamic correction $\alpha = [(\partial \ln a/\partial \ln x)]_{T,P}$; a is the activity, and x is the mole fraction. From the Gibbs-Duhem equation, the derivative $(\partial \ln a/\partial \ln x)$ is the same whether written for A or B.

Several liquid models purport to relate D_{AB} to composition; e.g., the Darken equation [48, 75] predicts that

$$D_{AB} = (D_A^* x_A + D_B^* x_B)\alpha \tag{11-10.1}$$

where D_A^* and D_B^* are tracer diffusion coefficients at x_A, x_B and α is evaluated at the same composition. Equation (11-10.1) was originally proposed to describe diffusion in metals, but it has been used for organic liquid mixtures by a number of investigators [31, 33, 74, 136, 148, 216, 219] with reasonable success except for mixtures in which the components may associate [89]. The unavailability of tracer diffusion coefficients in most instances has led to a modification of Eq. (11-10.1) as

$$D_{AB} = (D_{BA}^{\circ} x_A + D_{AB}^{\circ} x_B)\alpha = [x_A(D_{BA}^{\circ} - D_{AB}^{\circ}) + D_{AB}^{\circ}]\alpha \tag{11-10.2}$$

That is, D_{AB} is a linear function of composition (see Fig. 11-2) corrected by the thermodynamic factor α. Equation (11-10.2) is easier to use because the infinitely dilute diffusion coefficients D_{BA}° and D_{AB}° may be estimated by techniques shown in Sec. 11-9. The thermodynamic term in Eq. (11-10.2) often overcorrects D_{AB}. Rathbun and Babb [173] suggest α be raised to a fractional power; for associated systems, the exponent chosen was 0.6 unless there were *negative* deviations from Raoult's law when an exponent of 0.3 was recommended. It is interesting to note [179] that curves showing α and D_{AB} as a function of x_A tend to have the same curvature, thus providing some credence to the use of α as a correction factor.

Sanchez and Clifton [179] found they could correlate D_{AB} with composition for a wide variety of binary systems by using a modification of Eq. (11-10.2):

$$D_{AB} = (D_{BA}^{\circ} x_A + D_{AB}^{\circ} x_B)(1 - m + m\alpha) \tag{11-10.3}$$

where the parameter m is to be found from one mixture datum point, preferably in the midcompositional range. m varies from system to system and may be either greater or less than unity. When $m = 1$, Eq. (11-10.3) reduces to Eq. (11-10.2). Interestingly, for a number of highly associated systems, m was found to be between 0.8 and 0.9. The temperature dependence of m is not known.

Another theory predicts that the group $D_{AB}\eta/\alpha$ should be a linear function of mole fraction [8, 19, 26]. Vignes [219] shows graphs indicating this is not even approximately true for the systems acetone-water and acetone-chloroform. Rao and Bennett [170] studied several very nonideal mixtures and found that, while the group $D_{AB}\eta/\alpha$ did not vary appreciably with composition, no definite trends could be discerned. One of the systems studied (aniline–carbon tetrachloride) is shown in Fig. 11-9. In this case, D_{AB}, η, α, and $D_{AB}\eta$ varied widely; the group $D_{AB}\eta/\alpha$ also showed an unusual variation with composition. Carman and Stein [34] stated that $D_{AB}\eta/\alpha$ is a linear function of x_A for the nearly ideal system benzene–carbon tetrachloride and for the nonideal system acetone-chloroform but not for ethyl alcohol–water. Vignes [219] suggested a convenient way of correlating the composition effect on the liquid diffusion coefficient:

$$D_{AB} = [(D_{AB}^\circ)^{x_B}(D_{BA}^\circ)^{x_A}]\alpha \qquad (11\text{-}10.4)$$

and, therefore, a plot of log (D_{AB}/α) vs. mole fraction should be linear. He illustrated this relation with many systems, and, with the exception of strongly associated mixtures, excellent results were obtained. Figure 11-10 shows the same aniline–carbon tetrachloride system plotted earlier in Fig. 11-9. Although not perfect, there is a good agreement with Eq. (11-10.4).

Dullien [54] carried out a statistical test of the Vignes correlation. It was found to fit experimental data extremely well for ideal or nearly ideal mixtures, but there were several instances when it was not particularly accurate for nonideal, nonassociating solutions. Other authors report that Vignes correlation is satisfactory for benzene and n-heptane [30] and toluene and methylcyclohexane [86], not for benzene and cyclohexane [128].

The Vignes relation can be derived from absolute rate theory, and a logical modification of this equation is found to be [124]

$$D_{AB}\eta = [(D_{AB}^\circ\eta_B)^{x_B}(D_{BA}^\circ\eta_A)^{x_A}]\alpha \qquad (11\text{-}10.5)$$

A test of 11 systems showed that this latter form was marginally better in fitting experimental data. In Fig. 11-11 we have plotted both log $(D_{AB}\eta/\alpha)$ and log (D_{AB}/α) as a function of composition for the aniline-benzene
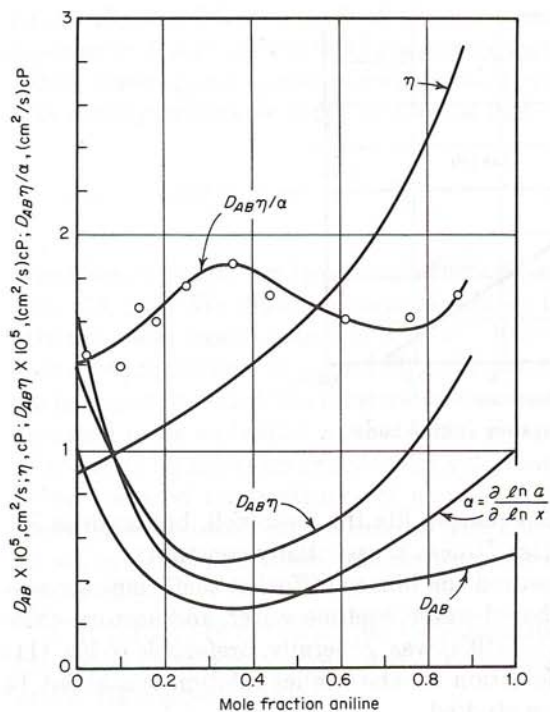
Figure 11-9 Diffusion coefficients for the system aniline–carbon tetrachloride at 298 K. *(From Ref. 170.)*
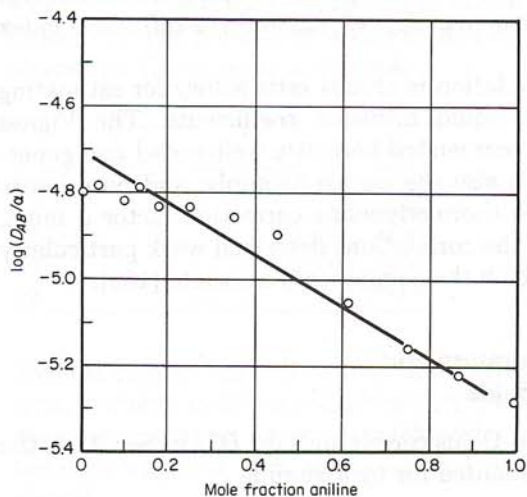
Figure 11-10 Vignes plot for the system aniline–carbon tetrachloride at 298 K.
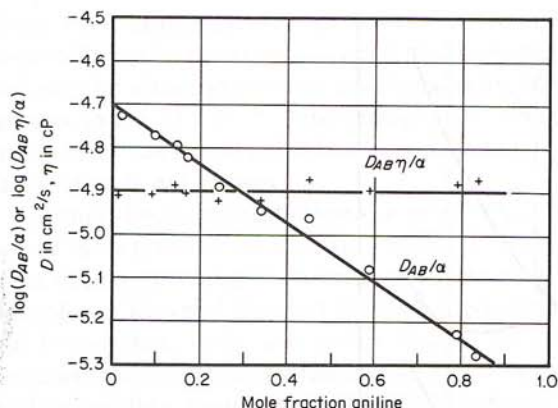
Figure 11-11 Vignes plot for the system aniline-benzene at 298 K. *(Data from Ref. 170.)*

system. The original Vignes equation fits the data well, but so does Eq. (11-10.5); in fact, for the latter $D_{AB}\eta/\alpha$ is essentially constant.

Tyn and Calus [213] measured the binary diffusion coefficient for several associating systems (ethanol-water, acetone-water, and acetone-chloroform) and found that Eq. (11-10.4) was, generally, preferable to Eq. (11-10.5), although the mean deviation for the Vignes relation was about 14 percent for the three systems studied.

Other correlation methods have been proposed [9, 40, 43, 72, 84, 87, 171, 205], but they are either less accurate or less general than those discussed above.

Baldauf and Knapp [15] present an exceptionally complete data set for eleven binary liquid mixtures giving D_{AB}, η_m, ρ_m, and the refractive index as a function of composition.

In summary, no single correlation is always satisfactory for estimating the concentration effect on liquid diffusion coefficients. The Vignes method [Eq. (11-10.4)] is recommended here as a well-tested and generally accurate correlation. It is also the easiest to apply, and no mixture viscosities are necessary. The thermodynamic correction factor α must, however, be known. None of the correlations described work particularly well for liquid mixtures in which the components associate [185].

11-11 The Effect of Temperature and Pressure on Diffusion in Liquids

For the Wilke-Chang and Tyn-Calus correlations for D_{AB}° in Sec. 11-9, the effect of temperature was accounted for by assuming

$$\frac{D_{AB}^\circ \eta_B}{T} = \text{constant} \qquad (11\text{-}11.1)$$

In the Hayduk-Minhas method, the (absolute) temperature was raised to a power > 1, and the viscosity parameter was a function of solute volume. While these approximations may be valid over small temperature ranges, it is usually preferable [180] to assume that

$$D_{AB} \text{ (or } D_{AB}^{o}) = A \exp \frac{-B}{T} \tag{11-11.2}$$

Equation (11-11.2) has been employed by a number of investigators [106, 137, 178, 209]. We illustrate its applicability in Fig. 11-12 with the system ethanol-water from about 298 K to 453 K for both infinitely dilute diffusion coefficients and D_{AB} for a 20 mole percent solution [117]. Note that we have not included the thermodynamic correction factor α because it is assumed to be embodied in the A and B parameters. Actually, since the viscosity of liquids is an exponentially decreasing function of temperature, below reduced temperatures of about 0.7, the product $D_{AB}\eta$ might be expected to be temperature-insensitive if the energies of activation for diffusion and viscosity were opposite in sign and of the same magnitude numerically.

Tyn [210, 211] reviewed the various proposed techniques to correlate infinitely dilute binary (and also self-) diffusion coefficients with temperature. He suggested that

$$\frac{D_{AB}^{o}(T_2)}{D_{AB}^{o}(T_1)} = \left(\frac{T_c - T_1}{T_c - T_2}\right)^n \tag{11-11.3}$$

where T_c is the critical temperature of the *solvent* B. T_c, T_1, and T_2 are in kelvins. The parameter n was related to the heat of vaporization of the solvent at T_b (solvent) as follows:

n	$\Delta H_v(T_b)$, J/mol
3	7,900 to 30,000
4	30,000 to 39,700
6	39,700 to 46,000
8	46,000 to 50,000
10	$>50,000$

Typical compounds falling into these categories would be $n = 3$, n-pentane, acetone, cyclohexane, chloroform; $n = 4$, benzene, toluene, chlorobenzene, n-octane, carbon tetrachloride; $n = 6$, cyclohexane, propanol, butanol, water; $n = 8$, heptanol; and $n = 10$, ethylene and propylene glycols.

Equation (11-11.3), which does not require mixture viscosity data, was tested with a large number of binary systems, and an error of about 9
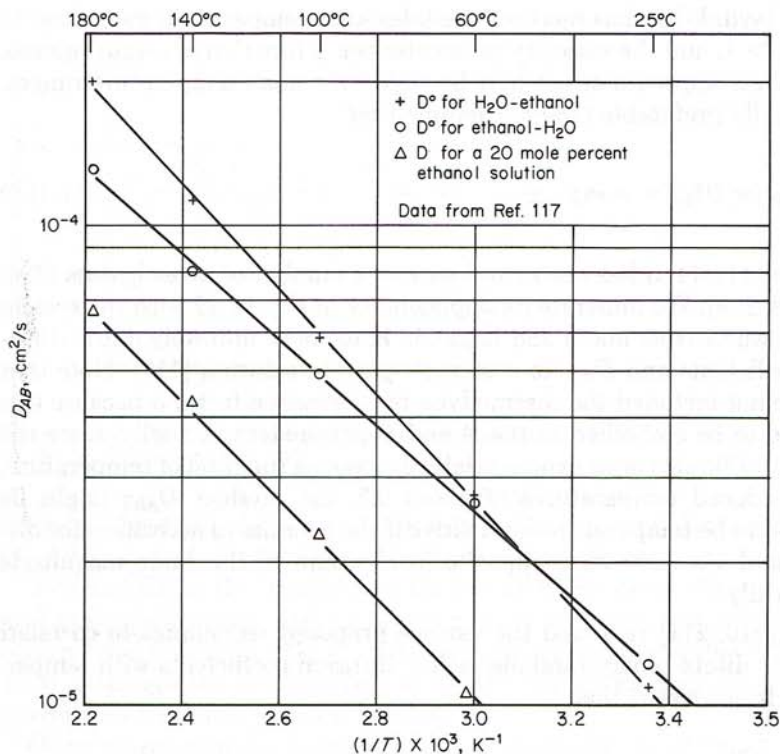
Figure 11-12 Variation of diffusion coefficients with temperature.

percent was found. When Eq. (11-11.1) also was examined, Tyn reported an error of about 10 percent. The temperature ranges for Eq. (11-11.3) are about 10 K above the freezing point to about 10 K below the normal boiling point. Larger errors were noted if these ranges were exceeded.

The effect of pressure on liquid diffusion coefficients has received little attention. Easteal [59] attempted to correlate tracer or self-diffusion coefficients with pressure and suggested

$$\ln D_j^* = a + bP^{0.75} \tag{11-11.4}$$

where D_j^* is a tracer or self-diffusion coefficient and a and b are constants for a given solute, but they do vary significantly with temperature. b is a negative number, and thus D_j^* decreases with an increase in pressure. As an example, the self-diffusion coefficient for n-hexane decreases from about 4.2×10^{-5} cm^2/s at 1 bar to about 0.7×10^{-5} cm^2/s at 3500 bar at a temperature of 298 K.

From Eq. (11-11.1), at a given temperature, it could be inferred that

$$D_{AB}^{\circ}\eta_B = \text{constant} \tag{11-11.5}$$

If solvent–liquid viscosity data were available at high pressures, it would then be possible to employ Eq. (11-11.5) to estimate D_{AB}° at the elevated pressure from low-pressure diffusion coefficient data. Dymond and Woolf [58] show, however, that this proportionality is only approximate for tracer-diffusion coefficients, but they indicate it may be satisfactory for binaries with large solute molecules.

11-12   Diffusion in Multicomponent Liquid Mixtures

In a binary liquid mixture, as indicated in Secs. 11-2 and 11-8, a single diffusion coefficient was sufficient to express the proportionality between the flux and concentration gradient. In multicomponent systems, the situation is considerably more complex, and the flux of a given component depends upon the gradient of $n - 1$ components in the mixture. For example, in a ternary system of A, B, and C, the flux of A can be expressed as

$$J_A = \mathbf{D}_{AA}\frac{dc_A}{dz} + \mathbf{D}_{AB}\frac{dc_B}{dz} \tag{11-12.1}$$

Similar relations can be written for J_B and J_C. The coefficients $\mathbf{D}_{AA}$ and $\mathbf{D}_{BB}$ are called *main coefficients;* they are *not* self-diffusion coefficients. $\mathbf{D}_{AB}$, $\mathbf{D}_{BA}$, etc., are *cross-coefficients,* because they relate the flux of a component i to a gradient in j. $\mathbf{D}_{ij}$ is normally not equal to $\mathbf{D}_{ji}$ for multicomponent systems.

Frames of reference in multicomponent systems must be clearly defined. Yon and Toor [235] discuss some limitations in this context.

One important case of multicomponent diffusion results when a solute diffuses through a homogeneous solution of mixed solvents. When the solute is dilute, there are no concentration gradients for the solvent species and one can speak of a single solute diffusivity with respect to the mixture D_{Am}°. This problem has been discussed by several authors [46, 102, 167, 203], and empirical relations for D_{Am}° have been proposed. Perkins and Geankoplis [167] evaluated several methods and suggested

$$D_{Am}^{\circ}\eta_m^{0.8} = \sum_{\substack{j=1 \\ j\neq A}}^{n} x_j D_{Aj}^{\circ}\eta_j^{0.8} \tag{11-12.2}$$

where D_{Am}° = *effective* diffusion coefficient for a dilute solute A into the mixture, cm^2/s

D_{Aj}° = infinite dilution binary diffusion coefficient of solute A into the solvent j, cm^2/s

x_j = mole fraction of j

η_m = mixture viscosity, cP

η_j = pure component viscosity, cP

When tested with data for eight ternary systems, errors were normally less than 20 percent, except for cases involving CO_2. These same authors also suggested that the Wilke-Chang equation (11-9.1) might be modified to include the mixed solvent case, i.e.,

$$D_{Am}^{\circ} = 7.4 \times 10^{-8} \frac{(\phi M)^{1/2} T}{\eta_m V_A^{0.6}}$$
(11-12.3)

$$\phi M = \sum_{\substack{j=1 \\ j \neq A}}^{n} x_j \phi_j M_j$$
(11-12.4)

Although not extensively tested, Eq. (11-12.3) provides a rapid, reasonably accurate estimation method.

For CO_2 as a solute diffusing into mixed solvents, Takahashi et al. [202] recommend

$$D^{\circ}(CO_2 \text{-} m) \left(\frac{\eta_m}{V_m}\right)^{1/3} = \sum_{\substack{j=1 \\ j \neq CO_2}}^{n} x_j D^{\circ}(CO_2 \text{-} j) \left(\frac{\eta_j}{V_j}\right)^{1/3}$$
(11-12.5)

where V_m is the molar volume, cm^3/mol, for the mixture at T and V_j applies to the pure component. Tests with a number of ternary systems involving CO_2 led to deviations from experimental values usually less than 4 percent.

Example 11-8 Estimate the diffusion coefficient of acetic acid diffusing into a mixed solvent containing 20.7 mole percent ethyl alcohol in water. The acetic acid concentration is small. Assume the temperature is 298 K.

data Let E = ethyl alcohol, W = water, and A = acetic acid. At 298 K, η_E = 1.10 cP, η_W = 0.894 cP, D_{AE} = 1.03×10^{-5} cm^2/s, D_{AW} = 1.30×10^{-5} cm^2/s, and for the solvent mixture under consideration, η_m = 2.35 cP.

solution From Eq. (11-12.2)

$$D_{Am}^{\circ} = (2.35)^{-0.8}[(0.207)(1.03 \times 10^{-5})(1.10)^{0.8}$$
$$+ (0.793)(1.30 \times 10^{-5})(0.894)^{0.8}]$$
$$= 0.59 \times 10^{-5} \ cm^2/s$$

The experimental value reported by Perkins and Geankoplis is 0.571×10^{-5} cm^2/s. Note that this value is significantly below the two limiting binary values. The decrease in the mixture diffusivity appears to be closely related to the increase in solvent mixture viscosity relative to the pure components. Had the modified Wilke-Chang equation been used, with $V_A = 64.1$ cm^3/mol (Table 3-8), $\phi_E = 1.5$, and $\phi_W = 2.6$, and with $M_E = 46$ and $M_W = 18$, using Eqs. (11-12.3) and (11-12.4),

$$\phi M = (0.207)(1.5)(46) + (0.793)(2.6)(18) = 51.39$$

$$D^o_{A_m} = \frac{(7.4 \times 10^{-8})(51.39)^{1/2}(298)}{(2.35)(64.1)^{0.6}}$$

$$= 0.55 \times 10^{-5} \ cm^2/s$$

Example 11-9 Estimate the diffusion coefficient of CO_2 (D) into a mixed solvent of n-octanol (L) and carbon tetrachloride (C) containing 60 mole percent n-octanol. The temperature is 298 K.

data From Ref. 202, $D^o_{DL} = 1.53 \times 10^{-5}$ cm^2/s, $D^o_{DC} = 3.17 \times 10^{-5}$ cm^2/s, $\eta_m = 3.55$ cP, $\eta_L = 7.35$ cP, and $\eta_C = 0.88$ cP. With densities and molecular weights given in Appendix A, $V_L = 158$ cm^3/mol and $V_C = 97.1$ cm^3/mol at 298 K. The mixture volume is not known. If we assume that the mole fraction of CO_2 in the liquid mixture is small and that n-octanol and carbon tetrachloride form ideal solutions,

$$V_m \approx (0.6)(158) + (0.4)(97.1) = 133.6 \ cm^3/mol$$

solution With Eq. (11-12.5)

$$\begin{aligned} D^o \ (CO_2\text{-}m) &= (3.55/133.6)^{-1/3} \ [(0.6)(1.53 \times 10^{-5})(7.35/158)^{1/3} \\ &\quad + (0.4)(3.17 \times 10^{-5}) \ (0.88/97.1)^{1/3}] \\ &= 1.99 \times 10^{-5} \ cm^2/s \end{aligned}$$

The experimental value [202] is 1.96×10^{-5} cm^2/s.

When dealing with the general case of multicomponent diffusion coefficients, there are no convenient and simple estimation methods. Cullinan [42, 45] has discussed the possibility of adapting the Vignes correlation [Eq. (11-10.4)] to ternary systems, but the requirement for extensive thermodynamic activity data for the mixture has severely limited the applicability of the method. Kett and Anderson [114, 115] apply hydrodynamic theory to estimate ternary diffusion coefficients. Although some success was achieved, the method again requires extensive data on activities, pure component and mixture volumes, and viscosities, as well as tracer and binary diffusion coefficients. Bandrowski and Kubaczka [16] suggest using the mixture critical volume as a correlating parameter to estimate D_{A_m} for multicomponent mixtures.

Other authors [25, 32, 44, 125, 152, 153] also have discussed the problem of obtaining multicomponent liquid diffusion coefficients.

11-13   Diffusion in Electrolyte Solutions

When a salt dissociates in solution, ions rather than molecules diffuse. In the absence of an electric potential, however, the diffusion of a single salt may be treated as molecular diffusion.

The theory of diffusion of salts at low concentrations is well developed. At concentrations encountered in most industrial processes, one normally resorts to empirical corrections, with a concomitant loss in generality and accuracy. A comprehensive discussion of this subject is available [159].

For dilute solutions of a *single* salt, the diffusion coefficient is given by the Nernst-Haskell equation

$$D_{AB}^\circ = \frac{RT[(1/n_+) + (1/n_-)]}{F^2[(1/\lambda_+^\circ) + (1/\lambda_-^\circ)]} \tag{11-13.1}$$

where D_{AB}° = diffusion coefficient at infinite dilution, based on molecular concentration, cm^2/s

T = temperature, K

R = gas constant, 8.314 J/(mol·K)

$\lambda_+^\circ, \lambda_-^\circ$ = limiting (zero concentration) ionic conductances, (A/cm^2) (V/cm)(g-equiv/cm^3)

n_+, n_- = valences of cation and anion, respectively

F = faraday = 96,500 C/g-equiv

TABLE 11-6   Limiting Ionic Conductances in Water at 298 K [90]
(A/cm^2)(V/cm)(g-equiv/cm^3)

Anion	γ_-°	Cation	γ_+°
OH$^-$	197.6	H$^+$	349.8
Cl$^-$	76.3	Li$^+$	38.7
Br$^-$	78.3	Na$^+$	50.1
I$^-$	76.8	K$^+$	73.5
NO$_3^-$	71.4	NH$_4^+$	73.4
ClO$_4^-$	68.0	Ag$^+$	61.9
HCO$_3^-$	44.5	Tl$^+$	74.7
HCO$_2^-$	54.6	(1/2)Mg^{2+}	53.1
CH$_3$CO$_2^-$	40.9	(1/2)Ca^{2+}	59.5
ClCH$_2$CO$_2^-$	39.8	(1/2)Sr^{2+}	50.5
CNCH$_2$CO$_2^-$	41.8	(1/2)Ba^{2+}	63.6
CH$_3$CH$_2$CO$_2^-$	35.8	(1/2)Cu^{2+}	54
CH$_3$(CH$_2$)$_2$CO$_2^-$	32.6	(1/2)Zn^{2+}	53
C$_6$H$_5$CO$_2^-$	32.3	(1/3)La^{3+}	69.5
HC$_2$O$_4^-$	40.2	(1/3)Co(NH$_3$)$_6^{3+}$	102
(1/2)C$_2$O$_4^{2-}$	74.2		
(1/2)SO$_4^{2-}$	80		
(1/3)Fe(CN)$_6^{3-}$	101		
(1/4)Fe(CN)$_6^{4-}$	111		

Values of λ_+° and λ_-° can be obtained for many ionic species at 298 K from Table 11-6 or from alternative sources [149, 177]. If values of λ_+° and λ_-° at other temperatures are needed, an approximate correction factor is $T/334\eta_W$, where η_W is the viscosity of water at T in centipoises.

As the salt concentration becomes finite and increases, the diffusion coefficient decreases rapidly and then usually rises, often becoming greater than D_{AB}° at high normalities. Figure 11-13 illustrates the typical trend for three simple salts. The initial decrease at low concentrations is proportional to the square root of the concentration, but deviations from this trend are usually significant above 0.1 N.

No reliable method has yet been proposed to relate D_{AB}° to concentration. Gordon [79], however, has proposed an empirical equation which has been applied to systems at concentrations up to 2 N:

$$D_{AB} = D_{AB}^\circ \frac{\eta_S}{\eta} (\rho_S \overline{V}_S)^{-1} \left(1 + m \frac{\partial \ln \gamma_\pm}{\partial m}\right) \tag{11-13.2}$$

where D_{AB}° = diffusion coefficient at infinite dilution, [Eq. (11-13.1)], cm²/s

ρ_S = molar density of the solvent, mol/cm³
$\overline{V}_S$ = partial molar volume of the solvent, cm³/mol
η_S = viscosity of the solvent, cP
η = viscosity of the solution, cP
m = molality of the solute, mol/kg solvent
$\gamma_\pm$ = mean ionic activity coefficient of the solute

In many cases, the product $\rho_S \overline{V}_S$ is close to unity, as is the viscosity ratio η_S/η, so that Gordon's relation provides an activity correction to the diffusion coefficient at infinite dilution. Though Harned and Owen [90] tabulate $\gamma_\pm$ as a function of m for many aqueous solutions, there now exist
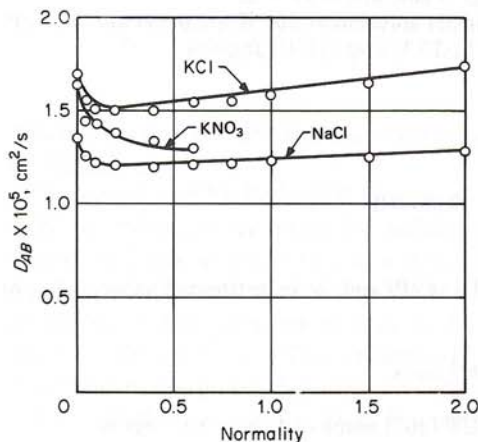
Figure 11-13 Effect of concentration on diffusivity of electrolytes in aqueous solution at 18.5°C. Solid lines calculated by using Eq. (11-13.2); data from Ref. 79.

several semiempirical correlation techniques to relate $\gamma_{\pm}$ to concentration. Bromley [23] presents an analytical relation, and Meissner et al. [141 to 145] show generalized graphical correlations. The solid lines in Fig. 11-13 were calculated from Eq. (11-13.2).

Data on the diffusion of CO_2 into electrolyte solutions have been reported by Ratcliff and Holdcroft [171]. The diffusion coefficient was found to decrease linearly with an increase in salt concentration.

In summary, for very dilute solutions of electrolytes, employ Eq. (11-13.1). When values of the limiting ionic conductances in water are not available at the desired temperature, use those in Table 11-6 for 298 K and multiply D_{AB}° at 298 K by $T/334\eta_W$, where η_W is the viscosity of water at T in centipoises.

For concentrated solutions, use Eq. (11-13.2). If values of $\gamma_{\pm}$ and λ° are not available at T, calculate D_{AB} at 298 K and multiply it by $(T/298)[(\eta$ at $298)/(\eta$ at $T)]$. If necessary, the ratio of the solution viscosity at 298 K to that at T may be assumed to be the same as the corresponding ratio for water.

Example 11-10 Estimate the diffusion coefficient of NaOH in a 2 N aqueous solution at 288 K.

solution From data on densities of aqueous solutions of NaOH, it is evident that, up to 12 weight percent NaOH (about 3 N), the density increases almost exactly in inverse proportion to the weight fraction of water; i.e., the ratio of moles of water per liter is essentially constant at 55.5. Thus both V/n and $\overline{V}_1$ are very nearly 55.5 and cancel in Eq. (11-13.2). In this case, the molality m is essentially identical with the normality.

In plotting the values of $\gamma_{\pm}$ for NaOH at 298 K [90] vs. molality m, the slope at $2m$ is approximately 0.047. Hence

$$m\frac{\partial \ln \gamma_{\pm}}{\partial m} = \frac{m}{\gamma_{\pm}}\frac{\partial \gamma_{\pm}}{\partial m} = \frac{2}{0.698}(0.047) = 0.135$$

The value 0.698 is the mean activity coefficient at $m = 2$.

The viscosities of water and 2 N NaOH solution at 298 K are 0.894 and 1.42 cP, respectively. Substituting in Eqs. (11-13.1) and (11-13.2) gives

$$D_{AB}^{\circ} = \frac{(2)(8.314)(298)}{[(1/50) + (1/198)](96,500)^2}$$

$$= 2.12 \times 10^{-5} \text{ cm}^2/\text{s}$$

$$D_{AB} = (2.12 \times 10^{-5})\frac{0.894}{1.42}\frac{55.5}{55.5}[1 + (2)(0.135)]$$

$$= 1.70 \times 10^{-5} \text{ cm}^2/\text{s at 298 K}$$

At 288 K, the viscosity of water is 1.144 cP, and so the estimated value of D_{AB} at 288 K is

$$1.70 \times 10^{-5}\frac{(288)}{(334)(1.144)} = 1.28 \times 10^{-5} \text{ cm}^2/\text{s}$$

which may be compared with the ICT [107] value of $1.36 \times 10^{-5} \text{ cm}^2/\text{s}$.

In a system of *mixed electrolytes,* such as in the simultaneous diffusion of HCl and NaCl in water, the faster-moving H^+ ion may move ahead of its Cl^- partner, the electric current being maintained at zero by the lagging behind of the slower-moving Na^+ ions. In such systems, the unidirectional diffusion of each ion species results from a combination of electric and concentration gradients:

$$N_+ = \frac{\gamma_+}{F^2}\left(-RT\frac{\partial c_+}{\partial z} - Fc_+\frac{\partial E}{\partial z}\right) \qquad (11\text{-}13.3)$$

$$N_- = \frac{\gamma_-}{F^2}\left(-RT\frac{\partial c_-}{\partial z} - Fc_-\frac{\partial E}{\partial z}\right) \qquad (11\text{-}13.4)$$

where N_+, N_- = diffusion flux densities of the cation and anion, respectively, g-equiv/cm^2·s

c_+, c_- = corresponding ion concentrations, g-equiv/cm^3

$\partial E/\partial z$ = gradient in electric potential

The electric field gradient may be imposed externally but is present in the ionic solution even if, owing to the small separation of charges which result from diffusion itself, there is no external electrostatic field. Collision effects, ion complexes, and activity corrections are neglected.

One equation for each cation and one for each anion can be combined with the requirement of zero current at any z to give $\Sigma N_+ = \Sigma N_-$. Solving for the unidirectional flux densities [172],

$$n_+N_+ = \frac{-RT\gamma_+}{F^2n_+}(G_+ - n_+c_+Y) \qquad (11\text{-}13.5)$$

$$n_-N_- = \frac{-RT\gamma_-}{F^2n_-}(G_- + n_-c_-Y) \qquad (11\text{-}13.6)$$

$$Y = \frac{(\Sigma\gamma_+G_+/n_+) - (\Sigma\gamma_-G_-/n_-)}{\Sigma\gamma_+c_+ + \Sigma\gamma_-c_-} \qquad (11\text{-}13.7)$$

where G_+ and G_- are the concentration gradients $\partial c/\partial z$ in the direction of diffusion.

Vinograd and McBain [221] have used these relations to represent their data on diffusion in multi-ion solutions. D_{AB} for the hydrogen ion was found to decrease from 12.2 to 4.9×10^{-5} cm^2/s in a solution of HCl and $BaCl_2$ when the ratio of H^+ to Ba^{2+} was increased from zero to 1.3; D_{AB} at the same temperature is 9.03×10^{-5} for the free H^+ ion, and 3.3×10^{-5} for HCl in water. The presence of the slow-moving Ba^{2+} accelerates the H^+ ion, the potential existing with zero current causing it to move in dilute solution even faster than it would as a free ion with no other cation

present. That is, electrical neutrality is maintained by the hydrogen ions moving ahead of the chlorine, faster than they would as free ions, while the barium diffuses more slowly than as a free ion.

The interaction of ions in a multi-ion system is important when the several ion conductances differ greatly, as they do when H^+ or OH^- is diffusing. When the diffusion of one of these two ions is not involved, no great error is introduced by the use of "molecular" diffusion coefficients for the salt species present.

The relations proposed by Vinograd and McBain are not adequate to represent a ternary system, in which four independent diffusion coefficients must be known to predict fluxes. The subject of ion diffusion in multicomponent systems is covered in detail in the papers by Wendt [228] and Miller [146, 147] in which it is demonstrated how one can obtain multicomponent ion diffusion coefficients, although the data required are usually not available.

Notation

a_j	activity of component j
A_B	parameter in Table 11-4
c	concentration, mol/cm^3; c_j, for component j; c_+, c_-, ion concentrations
D_{AB}	binary diffusion coefficient of A diffusing into B, cm^2/s; D_{AB}°, at infinite dilution of A in B; $\mathbf{D}_{AB}$, cross-coefficient in multicomponent mixtures; D_{im}, of i into a homogeneous mixture; D_{AB}^+, at a low pressure
D_A^*	tracer-diffusion coefficient of A, cm^2/s
D_{AA}	self-diffusion coefficient of A, cm^2/s; $\mathbf{D}_{AA}$, main coefficient for A in multicomponent diffusion
E	electric potential
f_D	correction term in Eq. (11-3.1)
F	faraday = 96,500 C/g-equiv
G_+, G_-	$\partial c_+/\partial z$ and $\partial c_-/\partial z$
ΔH_v	heat of vaporization at the normal boiling point, J/mol
I_A	parameter in Table 11-4
J_A	flux of A, mol/(cm$^2 \cdot$s); J_A^M, flux relative to a plane of no net mole flow; J_A^V, flux relative to a plane of no net volume flow
k	Boltzmann's constant, 1.3805×10^{-23} J/K
m	molality of solute, mol/kg solvent; parameter in Eq. (11-10.3)

M_A	molecular weight of A, g/mol; M_{AB}, $2[(1/M_A) + (1/M_B)]^{-1}$
n	number density of molecules; parameter in Eq. (11-11.3)
n_+, n_-	valences of cation and anion, respectively
N_A	flux of A relative to a fixed coordinate plane, mol/(cm²·s)
N_+, N_-	diffusion flux of cation and anion, respectively
P	pressure, bar; P_c, critical pressure; P_r, P/P_c
$\mathbf{P}_j$	parachor of component j
q, Q	parameters in Eq. (11-9.14)
r	distance of separation between molecules, Å
r_A	molecular radius in the Stokes-Einstein equation
R	gas constant, 8.314 J/(mol·K)
S_A, S_B	parameters in Table 11-4
T	temperature, kelvins; T_b, at the normal boiling point (at 1 atm); T_c, critical temperature; T_r, T/T_c
V	volume, cm³/mol; V_b, at T_b; $\overline{V}_A$, partial molar volume of A
V_j	molar volume of component j at either T_b or T, cm³/mol
x_j	mole fraction of j
y_j	mole fraction of j
z	direction coordinate for diffusion

GREEK

α	$\partial \ln a/\partial \ln x$, Eq. (11-2.8); α_c, parameter in Eq. (11-9.7)
β	parameter in Eq. (11-9.13)
γ	activity coefficient; $\gamma_\pm$, mean ionic activity coefficient
$\gamma_+^\circ, \gamma_-^\circ$	limiting (zero concentration) ionic conductances, (A/cm²)(V/cm) (g-equiv/cm³)
δ	polar parameter defined in Eq. (11-3.8)
ϵ	characteristic energy parameter; ϵ_A, for pure A; ϵ_{AB}, for an A-B interaction
ϵ, ϵ^*	parameters in Eqs. (11-9.8) and (11-9.9)
η	viscosity, cP; η_A, for pure A; η_m, for a mixture
μ_A	chemical potential of A, J/mol
μ_p	dipole moment, debyes
ρ	density, g/cm³
σ	characteristic length parameter, Å; σ_A, for pure A; σ_{AB}, for an A-B interaction; surface tension

Σ_v	Fuller et al. volume parameter, Table 11-1
ϕ	association parameter for the solvent, Eq. (11-9.1)
ψ	intermolecular potential energy of interaction
Ω_D	collision integral for diffusion

SUPERSCRIPTS

°	infinite dilution
*	tracer value
+	low pressure

SUBSCRIPTS

A, B	components A and B; usually B is the solvent
m	mixture
w	water
s	solvent

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12

Surface Tension

12-1 Scope

The surface tensions of both pure liquids and liquid mixtures are considered in this chapter. For the former, methods based on the law of corresponding states and upon the parachor are judged most accurate when estimated values are compared with experimental determinations. For mixtures, extensions of the pure component methods are presented, as is a method based upon a thermodynamic analysis of the system. Interfacial tensions for liquid-liquid or liquid-solid systems are not included.

12-2 Introduction

The boundary layer between a liquid phase and a gas phase may be considered a third phase with properties intermediate between those of a liquid and a gas. A qualitative picture of the microscopic surface layer shows that there are unequal forces acting upon the molecules; i.e., at low gas densities, the surface molecules are attracted sidewise and toward the bulk liquid but experience less attraction in the direction of the bulk gas. Thus the surface layer is in tension and tends to contract to the smallest area compatible with the mass of material, container restraints, and external forces, e.g., gravity.

A quantitative index of this tension can be presented in various ways; the most common is the surface tension σ, defined as the force exerted in the plane of the surface per unit length. We can consider a reversible isothermal process whereby surface area A is increased by pulling the surface apart and allowing the molecules from the bulk liquid to enter at constant temperature and pressure. The differential reversible work is $\sigma \, dA$; in this case σ is the surface Gibbs energy per unit of area. As equilibrium systems tend to a state of minimum Gibbs energy, the product σA also tends to a minimum. For a fixed σ, equilibrium is a state of minimum area consistent with the restraints of the system.

Surface tension is usually expressed in dynes per centimeter; surface Gibbs energy per unit area has units of ergs per square centimeter. These units and numerical values of σ are identical. In SI units, 1 erg/cm^2 = 1 mJ/m^2 = 1 mN/m.

The thermodynamics of surface layers furnishes a fascinating subject for study. Guggenheim [23], Gibbs [20], and Modell and Reid [43] have formulated treatments which differ considerably but reduce to similar equations relating macroscopically measurable quantities. In addition to the thermodynamic aspect, treatments of the physics and chemistry of surfaces have been published [1, 3, 4, 8, 57]. These subjects are not covered here; instead, the emphasis is placed upon the few reliable methods available to estimate σ from either semitheoretical or empirical equations.

12-3 Estimation of the Surface Tension of a Pure Liquid

As the temperature is raised, the surface tension of a liquid in equilibrium with its own vapor decreases and becomes zero at the critical point [53]. In the reduced-temperature range 0.45 to 0.65, σ for most organic liquids ranges from 20 to 40 dyn/cm, but for some low-molecular-weight dense liquids such as formamide, $\sigma > 50$ dyn/cm. For water $\sigma = 72.8$ dyn/cm at 293 K, and for liquid metals σ is between 300 and 600 dyn/cm; e.g., mercury at 293 K has a value of about 476.

A recent, thorough critical evaluation of experimental surface tensions has been prepared by Jasper [32]. Additional data are given in Ref. 35.

Essentially all useful estimation techniques for the surface tension of a liquid are empirical. Only two are discussed in any detail here, although others are briefly noted at the end of this section.

Macleod-Sugden correlation

Macleod [38] in 1923 suggested a relation between σ and the liquid and vapor densities:

$$\sigma^{1/4} = [P](\rho_L - \rho_v) \tag{12-3.1}$$

TABLE 12-1   Comparison of Calculated and Experimental Values of Surface Tension of Pure Liquids

Compound	T, K	σ (exp.),† dyn/cm	Macleod and Sugden, Eq. (12-3.1)	Brock and Bird, Eq. (12-3.6)
			Percent Error in Method‡	
Acetic acid	293	27.59	−4.6	
	333	23.62	−3.2	
Acetone	298	24.02	−5.4	2.4
	308	22.34	−3.9	3.7
	318	21.22	−4.5	2.7
Aniline	293	42.67	−3.2	11
	313	40.50	−6.0	10
	333	38.33	−7.1	9.1
	353	36.15	−8.8	8.0
Benzene	293	28.88	−5.1	−2.0
	313	26.25	−5.6	−1.9
	333	23.67	−5.0	−0.4
	353	21.20	−3.9	−1.9
Benzonitrile	293	39.37	−2.0	1.2
	323	35.89	−3.4	1.1
	363	31.26	−4.2	1.3
Bromobenzene	293	35.82	−0.7	−0.2
	323	32.34	−1.4	0
	373	26.54	−0.7	0.7
n-Butane	203	23.31	11	1.6
	233	19.69	5.2	0.9
	293	12.46	1.5	0.9
Carbon disulfide	293	32.32	3.8	3.0
	313	29.35	3.8	3.1
Carbon tetrachloride	288	27.65	−1.1	−4.9
	308	25.21	−1.2	−5.1
	328	22.76	−1.0	−5.0
	348	20.31	0.1	−4.9
	368	17.86	2.5	−4.4
Chlorobenzene	293	33.59	−0.6	−1.7
	323	30.01	0.7	−1.7
	373	24.06	5.8	−1.2
p-Cresol	313	34.88	0.5	
	373	29.32	−0.3	
Cyclohexane	293	25.24	−3.9	−4.8
	313	22.87	−3.5	−4.5
	333	20.49	−2.2	−4.3
Cyclopentane	293	22.61	−5.6	−2.0
	313	19.68	−2.4	0.1
Diethyl ether	288	17.56	0	0
	303	16.20	0.4	−2.5
2,3-Dimethylbutane	293	17.38	−0.9	−0.2
	313	15.38	0.6	−0.5
Ethyl acetate	293	23.97	−4.6	1.1
	313	21.65	−4.8	0
	333	19.32	−4.3	−0.9
	353	17.00	−2.7	−1.4
	373	14.68	0.5	−2.0

Compound	T, K	σ (exp.),† dyn/cm	Percent Error in Method‡	
			Macleod and Sugden, Eq. (12-3.1)	Brock and Bird, Eq. (12-3.6)
Ethyl benzoate	293	35.04	−1.9	2.7
	313	32.92	−2.7	2.9
	333	30.81	−3.1	2.9
Ethyl bromide	283	25.36	−5.3	15
	303	23.04	−6.1	13
Ethyl mercaptan	288	23.87	−6.7	3.5
	303	22.68	−9.1	−1.2
Formamide	298	57.02	−8.8	§
	338	53.66	−15	
	373	50.71	−20	
n-Heptane	293	20.14	−0.6	0.3
	313	18.18	0.7	0.1
	333	16.22	3.1	0.3
	353	14.26	6.8	0.8
Isobutyric acid	293	25.04	1.2	
	313	23.20	0.5	
	333	21.36	−1.2	
	363	18.60	−3.5	
Methyl formate	293	24.62	−7.6	4.4
	323	20.05	−7.2	4.6
	373	12.90	−7.4	4.3
	423	6.30	−8.8	5.4
	473	0.87	−14	21
Methyl alcohol	293	22.56	−13	
	313	20.96	−15	
	333	19.41	−17	
Phenol	313	39.27	−6.7	
	333	37.13	−7.3	
	373	32.86	−7.8	
n-Propyl alcohol	293	23.71	−0.6	
	313	22.15	−1.9	
	333	20.60	−3.3	
	363	18.27	−4.0	
n-Propyl benzene	293	29.98	0.2	−1.1
	313	26.83	0.8	−0.7
	333	24.68	2.1	−0.1
	353	22.53	3.9	0.7
	373	20.38	6.6	1.9
Pyridine	293	37.21	−2.8	−0.4
	313	34.60	−3.6	−0.8
	333	31.98	−4.1	−1.2

†Experimental values from Ref. 32, except for methyl formate, experimental values for which were taken from Ref. 38. Surface tensions quoted by Jasper are smoothed values obtained after plotting σ vs. T. Normally a linear relation was assumed over small temperature ranges. See discussion with Eq. (12-4.2).

‡Error = [(calc. − exp.)/exp.] × 100.

§Critical properties not known.

Sugden [67, 68] has called the temperature-independent parameter [P] the *parachor* and indicated how it might be estimated from the structure of the molecule. Quayle [50] employed experimental surface tension and density data for many compounds and calculated parachors. From these, he suggested an additive scheme to correlate [P] with structure, and a modified list of his values is shown in Table 11-3. When [P] values determined in this manner are used, the surface tension is given in dynes per centimeter and the densities are expressed in moles per cubic centimeter. The method is illustrated in Example 12-1, and calculated values of σ are compared with experimental surface tensions in Table 12-1.

Example 12-1 Use the Macleod-Sugden correlation to estimate the surface tension of isobutyric acid at 333 K. The experimental value quoted by Jasper [32] is 21.36 dyn/cm.

solution At 333 K, the liquid density is 0.912 g/cm^3 [31], and, with $M = 88.107$, $\rho_L = 0.912/88.107 = 1.035 \times 10^{-2}$ mol/cm^3. At 333 K, isobutyric acid is well below the boiling point, and at this low pressure $\rho_v \ll \rho_L$ and the vapor density term is neglected.
To determine the parachor from Table 11-3,

$$[P] = CH_3 - CH(CH_3) - + - COOH$$
$$= 133.3 + 73.8 = 207.1$$

Then, with Eq. (12-3.1),

$$\sigma = [(207.1)(1.035 \times 10^{-2})]^4 = 21.10 \text{ dyn/cm}$$
$$\text{Error} = \frac{21.10 - 21.36}{21.36} \times 100 = -1.2\%$$

Since σ is proportional to $([P]_{\rho_L})^4$, Eq. (12-3.1) is *very* sensitive to the values of the parachor and liquid density chosen. It is remarkable that the estimated values are as accurate as shown in Table 12-1.

Instead of employing experimental densities, correlations relating ρ to T, given in Chap. 3, may be used. One technique not covered in that chapter is given by Goldhammer [21] and discussed by Gambill [19]:

$$\rho_L - \rho_v = \rho_{Lb} \left(\frac{1 - T_r}{1 - T_{br}} \right)^n \tag{12-3.2}$$

ρ_{Lb} is the molal liquid density at the normal boiling point in moles per cubic centimeter. The exponent n ranges from 0.25 to 0.31; Fishtine [17] suggests the following values:

	n
Alcohols	0.25
Hydrocarbons and ethers	0.29
Other organic compounds	0.31

With Eq. (12-3.2), Eq. (12-3.1) becomes

$$\sigma = ([P]\rho_{Lb})^4 \left(\frac{1 - T_r}{1 - T_{br}}\right)^{4n} \tag{12-3.3}$$

where $4n$ varies between 1.0 and 1.24. As shown later, other correlations predict a similar temperature dependence; that is, σ decreases with temperature at a rate somewhat exceeding that predicted by a linear relation.

Corresponding states correlation

The group $\sigma/P_c^{2/3}T_c^{1/3}$ is dimensionless except for a numerical constant which depends upon the units of σ, P_c, and T_c.† Van der Waals suggested in 1894 [73] that this group could be correlated with $1 - T_r$. Brock and Bird [7] developed this idea for nonpolar liquids and proposed that

$$\frac{\sigma}{P_c^{2/3}T_c^{1/3}} = (0.132\alpha_c - 0.279)(1 - T_r)^{11/9} \tag{12-3.4}$$

where α_c is the Riedel parameter [55] at the critical point and α is defined as $d \ln P_{vp_r}/d \ln T_r$. Using a suggestion by Miller [42] to relate α_c to T_{br} and P_c,

$$\alpha_c = 0.9076 \left[1 + \frac{T_{br} \ln (P_c/1.01325)}{1 - T_{br}}\right] \tag{12-3.5}$$

it can be shown that

$$\sigma = P_c^{2/3}T_c^{1/3} Q(1 - T_r)^{11/9} \tag{12-3.6}$$

$$Q = 0.1196 \left[1 + \frac{T_{br} \ln (P_c/1.01325)}{1 - T_{br}}\right] - 0.279 \tag{12-3.7}$$

Equations (12-3.6) and (12-3.7) were used to compute σ values for nonpolar liquids in Table 12-1. The accuracy is similar to that for the Macleod-Sugden relation discussed earlier. However, the corresponding states method is not applicable to compounds exhibiting strong hydrogen-bonding (alcohols, acids) and quantum liquids (H_2, He, Ne).

A similar correlation was proposed by Riedel [56]. More recently, to

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†The fundamental dimensionless group is $\sigma V_c^{2/3}/RT_c$ [24, 74], but the proportionality $V_c \propto RT_c/P_c$ has been used and the gas constant has been dropped from the group.

broaden the approach to include polar liquids, Hakim et al. [26] introduced the Stiel polar factor, X, and proposed the following equation:

$$\sigma = P_c^{2/3} T_c^{1/3} Q_p \left(\frac{1 - T_r}{0.4}\right)^m \tag{12-3.8}$$

where σ = surface tension of polar liquid, dyn/cm
P_c = critical pressure, bar
T_c = critical temperature, K
$Q_p = 0.1560 + 0.365\omega - 1.754X - 13.57X^2 - 0.506\omega^2 + 1.287\omega X$
$m = 1.210 + 0.5385\omega - 14.61X - 32.07X^2 - 1.656\omega^2 + 22.03\omega X$
X = Stiel polar factor
ω = acentric factor, Sec. 2-3

Values of X can be estimated from the reduced vapor pressure at $T_r = 0.6$, $P_{vp_r}(0.6)$,

$$X = \log P_{vp_r}(0.6) + 1.70\omega + 1.552 \tag{12-3.9}$$

The general reliability of Eq. (12-3.8) is not known. The six constants in Q_p and m were obtained from data on only 16 polar compounds, some of which were only slightly polar (diethyl ether, dimethyl ether, ethyl mercaptan, acetone, etc.). X values are available for only a few substances, and estimated values of σ are sensitive to the value of X chosen.

Example 12-2 Using Eqs. (12-3.6) and (12-3.7), estimate the surface tension of liquid ethyl mercaptan at 303 K. The experimental value is 22.68 dyn/cm [32].

solution From Appendix A, for ethyl mercaptan, T_c = 499 K, T_b = 308.2 K, P_c = 54.9 bar. Thus T_{b_r} = 308.2/499 = 0.618. With Eq. (12-3.7)

$$Q = 0.1196 \left[1 + \frac{(0.618)\ln(54.9/1.01325)}{1 - 0.618}\right] - 0.279 = 0.613$$

$$\sigma = (54.9)^{2/3}(499)^{1/3}(0.613)\left(1 - \frac{303}{499}\right)^{11/9} = 22.4 \text{ dyn/cm}$$

$$\text{Error} = \frac{22.41 - 22.68}{22.68} \times 100 = -1.2\%$$

Other estimation methods

Statistical-mechanical theories of liquids yield reasonable results for surface tensions of simple liquids [48]. The surface tension has also been correlated with the molar refraction and refractive index [71], liquid compressibility [39, 58], and viscosity [9, 44, 47, 61, 72]. Schonhorn [61] expanded upon an earlier idea of Pelofsky [47] and showed that $\ln \sigma$ is linearly related to $(\eta_L - \eta_V)^{-1}$, where η is the viscosity. Rao et al. [51]

proposed a linear relation between log σ_b and T_{b_r} for different homologous series (σ_b is the surface tension at T_b) and Carey et al. [10] have related surface tension to parameters in the Peng-Robinson equation of state.

For rapid estimations of σ, nomographs have been presented [25, 46] for relating σ and T for hydrocarbons. Data for light hydrocarbons and their mixtures have been correlated by Porteous [49].

Surface tensions for several cryogenic liquids have been reported by Sprow and Prausnitz [64]; they were correlated by a modification of Eq. (12-3.4)

$$\sigma = \sigma_0(1 - T_r)^p \qquad (12\text{-}3.10)$$

where σ_0 and p were fitted to the data by a least-squares analysis. Values of p were close to $\frac{11}{9}$, but the best value of σ_0 was often slightly larger than $P_c^{2/3}T_c^{1/3}Q$, as predicted by Eq. (12-3.6).

Gray et al. [22] have correlated surface tensions of coal liquid fractions by

$$\sigma = P_c^{2/3}T_c^{1/3}(0.3993)(1 - T_r)^{0.4} \qquad (12\text{-}3.11)$$

Rice and Teja [54] have estimated surface tensions with a two-reference-fluid corresponding states method (see Secs. 3-7, 7-5, and 7-9), along with the assumption that the group $\sigma V_c^{2/3}/T_c$ varies linearly with the acentric factor. Murad [45] has used a shape factor approach (Sec. 10-3) to estimate surface tensions; several authors [33, 63] have proposed correlations which relate surface tension to the enthalpy of vaporization. None of these last methods appears to offer any significant advantage over the methods previously described.

Recommendations

For surface tensions of organic liquids, use the data collection of Jasper [32]. Two estimation methods were presented in this section, and calculated values are compared with experiment in Table 12-1. For non-hydrogen-bonded liquids, use the corresponding states method [Eqs. (12-3.6) and (12-3.7)]. The normal boiling point, critical temperature, and critical pressure are required. Errors are normally less than 5 percent.

For hydrogen-bonded liquids, use the Macleod-Sugden form [Eq. (12-3.1)] with the parachor determined from group contributions in Table 11-3. Either experimental saturated liquid and saturated vapor densities may be used or, with slightly less accuracy, the modified temperature form, Eq. (12-3.3), may be substituted. Errors are normally less than 5 to 10 percent.

If reliable values of ω and X are available, however, Eq. (12-3.8) is somewhat more accurate for alcohols.

12-4 Variation of Surface Tension with Temperature

Equation (12-3.3) indicates that

$$\sigma \propto (1 - T_r)^{4n} \tag{12-4.1}$$

where n varies from 0.25 to 0.31. In Fig. 12-1, $\log \sigma$ is plotted against $\log (1 - T_r)$ with experimental data for acetic acid, diethyl ether, and ethyl acetate. For the latter two, the slope is close to 1.25 for a value of $n = 0.31$; for acetic acid, the slope is 1.16 or $n = 0.29$. For most organic liquids, this encompasses the range normally found for n, although for alcohols, n may be slightly less. The corresponding states correlation predicts a slope of 1.22, giving $n = 0.305$.

For values of T_r between 0.4 and 0.7, Eq. (12-4.1) indicates that $d\sigma/dT$ is almost constant, and often the surface tension–temperature relation is represented by a linear equation

$$\sigma = a + bT \tag{12-4.2}$$

As an example, for nitrobenzene, between 313 and 473 K, data from Jasper [32] are plotted in Fig. 12-2. The linear approximation is satisfactory. Jasper lists values of a and b for many materials.

12-5 Surface Tensions of Nonaqueous Mixtures

The surface tension of a liquid mixture is not a simple function of the surface tensions of the pure components because, in a mixture, the composition of the surface is not the same as that of the bulk. In a typical situation, we know the bulk composition but not the surface composition.

The surface tension of a mixture σ_m is usually but not always [2, 77] less than that calculated from a mole fraction average of the surface tensions of the pure components. Also, the derivative $d\sigma_m/dx$ usually increases with composition for that component with the largest pure component surface tension.

The techniques suggested for estimating σ_m can conveniently be divided into two categories: those based on empirical relations suggested earlier for pure liquids and those derived from thermodynamics.
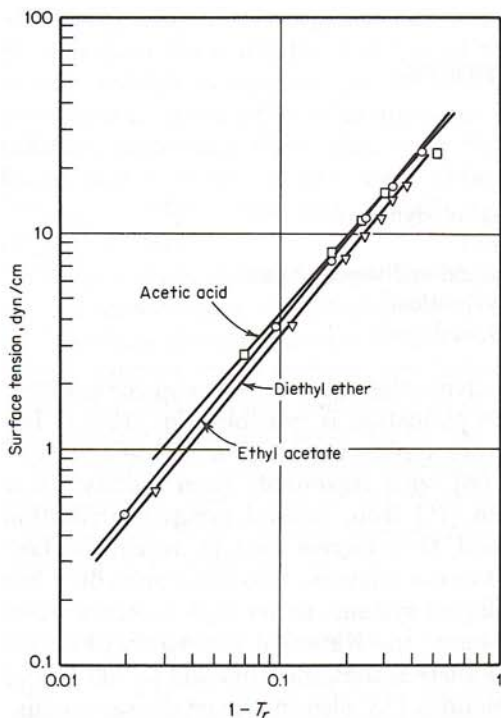
Figure 12-1 Variation of surface tension with temperature. *(Data from Ref. 38.)*
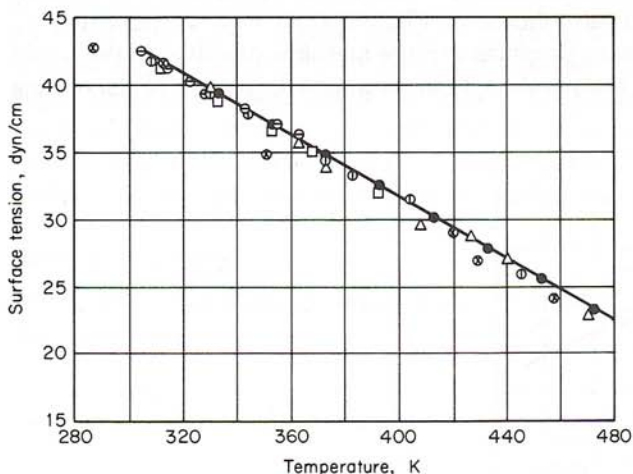
Figure 12-2 Surface tension of nitrobenzene: R. B. Badachhope, M. K. Gharpurey, and A. B. Biswas, *J. Chem. Eng. Data*, **10**:143 (1965); △ Ref. 68; ⊖ R. Kremann and R. Meirgast, *Monatsh. für Chemie*, **35**:1332 (1914); ⊝ F. M. Jaeger, *Z. Anorg. Allgem. Chem.*, **101**:1 (1917); □ W. Hückel and W. Jahnentz, *Chem. Ber.*, **75B**:1438 (1942); ⊗ W. Ramsay and J. Shields, *J. Chem. Soc.*, **63**:1089 (1893). *(From Ref. 32.)*

Macleod-Sugden correlation

Applying Eq. (12-3.1) to mixtures gives

$$\sigma_m^{1/4} = \sum_{i=1}^{n} [P_i](\rho_{L_m}x_i - \rho_{v_m}y_i) \qquad (12\text{-}5.1)$$

where σ_m = surface tension of mixture, dyn/cm
  $[P_i]$ = parachor of component i
  x_i, y_i = mole fraction of i in liquid and vapor phases
  ρ_{L_m} = liquid mixture density, mol/cm^3
  ρ_{v_m} = vapor mixture density, mol/cm^3

At low pressures, the term involving the vapor density and composition may be neglected; when this simplification is possible, Eq. (12-5.1) has been employed to correlate mixture surface tensions for a wide variety of organic liquids [6, 18, 27, 41, 56] with reasonably good results. Most authors, however, do not obtain $[P_i]$ from general group contribution tables such as Table 11-3; instead, they regress data to obtain the best value of $[P_i]$ for each component in the mixture. This same procedure has been used with success for gas-liquid systems under high pressure when the vapor term is significant. Weinaug and Katz [75] showed that Eq. (12-5.1) correlates methane-propane surface tensions from 258 to 363 K and from 2.7 to 103 bar. Deam and Maddox [13] also employed the same equation for the methane-nonane mixture from 239 to 297 K and 1 to 101 bar. Some smoothed data are shown in Fig. 12-3. At any temperature, σ_m decreases with increasing pressure as more methane dissolves in the liquid phase. The effect of temperature is more unusual; instead of decreasing
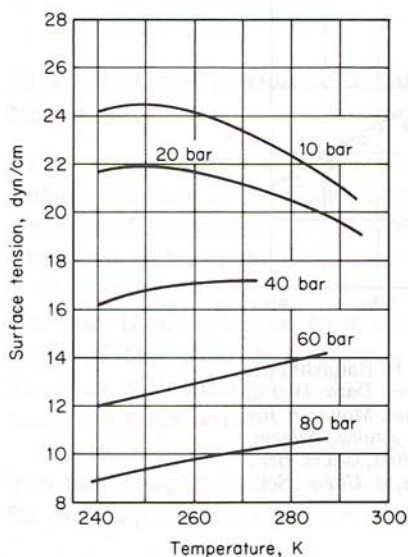
Figure 12-3 Surface tension for the system methane-nonane.

with rising temperature, σ_m increases, except at the lowest pressures. This phenomenon illustrates the fact that at the lower temperatures methane is more soluble in nonane and the effect of liquid composition is more important than the effect of temperature in determining σ_m.

When correlating these data with Eq. (12-5.1), Deam and Maddox found that the best results were obtained when $[P_{CH_4}] = 81.0$ and $[P_{C_9H_{20}}] = 387.6$. Note that if Table 11-3 is used, $[P_{CH_4}] = 71.0$ and $[P_{C_9H_{20}}] = 391$.

Other authors also have used Eq. (12-5.1) for correlating high-pressure surface tension data; e.g., Stegemeier† [66] studied the methane-pentane and methane-decane systems, Reno and Katz [52] studied the nitrogen-butane (and heptane) systems, and Lefrançois and Bourgeois [36] investigated the effect of rare-gas pressure on many organic liquids as well as the pressure of N_2 and H_2 on the surface tension of liquid ammonia.

When the Macleod-Sugden correlation is used, mixture liquid and vapor densities and compositions must be known. Errors at low pressures rarely exceed 5 to 10 percent and can be much less if $[P_i]$ values are obtained from experimental data.

Corresponding states correlation

Equation (12-3.6) has seen little application for mixtures because the composition of the surface is not the same as that of the bulk. Some mixing rule has to be assumed for P_{c_m}, T_{c_m}, and Q_m. A number of possible rules can be obtained from Chap. 4, or simple mole fraction averages can be used. A limited test of the latter technique for nonpolar mixtures indicated that the accuracy was of the same order as that obtained with the Macleod-Sugden mixture relation with $[P_i]$ values from Table 11-3. Murad [45] and Rice and Teja [54] have used their corresponding states methods to estimate mixture surface tensions.

Other empirical methods

Often, when only approximate estimates of σ_m are necessary, one chooses the general form

$$\sigma_m^r = \sum_{j=1}^n x_j \sigma_j^r \tag{12-5.2}$$

Hadden [25] recommends $r = 1$ for most hydrocarbon mixtures,‡ but much closer agreement is found if $r = -1$ to -3. Equation (12-5.1) may

---

†In this case, the exponent chosen for σ_m was $\frac{3}{11}$ rather than $\frac{1}{4}$.

‡In this reference, an empirical, *very* approximate method is suggested for mixtures when the temperature exceeds the critical temperature of at least one component.

also be written in a form similar to Eq. (12-5.2), using Eq. (12-3.1) to express the parachor $[P_i]$. Neglecting the vapor term (low pressures), we have

$$\sigma_m^{1/4} = \rho_{Lm} \sum_{i=1}^{n} \frac{x_i \sigma_i^{1/4}}{\rho_{Li}} \tag{12-5.3}$$

Equation (12-5.3) has an advantage over Eq. (12-5.1) in that, at the extremes of composition, it yields the correct values ($\sigma_m \to \sigma_i$ as $x_i \to 1.0$), whereas, depending upon the $[P_i]$ chosen, Eq. (12-5.1) may or may not reduce to the appropriate limiting value. The $\frac{1}{4}$ power on σ_i, however, is usually insufficient to provide the necessary curvature.

These empirical rules are illustrated in Example 12-3. The problem is that, with no theoretical basis, it is difficult to generalize, and although one rule may correlate data well for one system, it may fail on one quite similar. Figure 12-4 shows mixture surface tensions for several systems. All illustrate the nonlinearity of the σ_m-vs.-x relation but to different degrees. The surface tension of the acetophenone-benzene system is almost linear in composition, whereas the nitromethane-benzene and nitrobenzene-carbon tetrachloride systems are decidedly nonlinear and the diethyl ether-benzene case is intermediate.
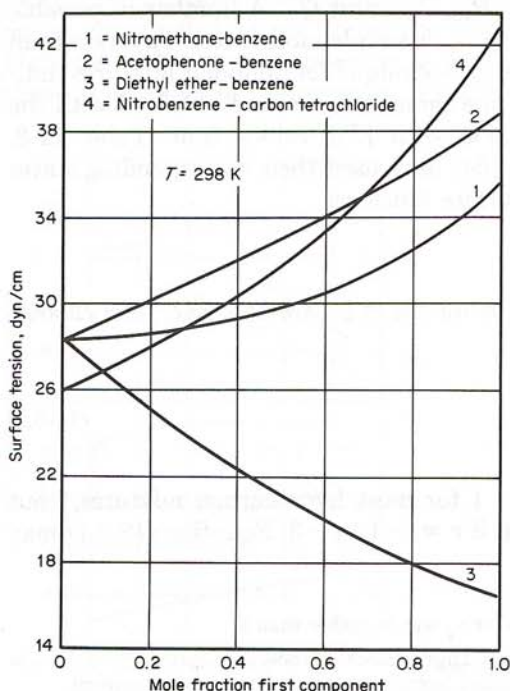
Figure 12-4 Mixture surface tensions. *(From Ref. 27.)*

Example 12-3 Estimate the surface tension of a mixture of diethyl ether and benzene containing 42.3 mole percent of the former. The temperature is 298 K. Hammick and Andrew [27] list densities and surface tensions for this system at 298 K; other data are from Appendix A.

	Benzene	Diethyl ether	Mixture with 42.3 mol % diethyl ether
Density, g/cm³	0.8722	0.7069	0.7996
Surface tension, dyn/cm	28.23	16.47	21.81
Molecular weight	78.114	74.123	76.426
Critical temperature, K	562.2	466.7	
Critical pressure, bar	48.9	36.4	
Normal boiling point, K	353.2	307.6	

solution MACLEOD-SUGDEN CORRELATION To employ Eq. (12-5.1), the parachors of benzene and diethyl ether are required. From Table 11-3,

$$[P_{\text{benzene}}] = C_6H_5- +H = 189.6 + 15.5 = 205.1$$
$$[P_{\text{ether}}] = (2)(CH_3-) + (2)(-CH_2-) + -O-$$
$$= (2)(55.5) + (2)(40.0) + 20.0 = 211$$
$$M_m = (0.423)(74.123) + (0.577)(78.114) = 76.426$$

When the vapor term is neglected, Eq. (12-5.1) becomes

$$\sigma_m^{1/4} = \frac{0.7996}{76.426}[(0.423)(211) + (0.577)(205.1)]$$

$$\sigma_m = 22.25 \text{ dyn/cm}$$

$$\text{Error} = \frac{22.25 - 21.81}{21.81} \times 100 = 2.0\%$$

With the parachor values estimated above and with pure component densities, Eq. (12-3.1) yields surface tensions of 27.5 dyn/cm for pure benzene and 16.40 dyn/cm for pure diethyl ether, compared with experimental values of 28.23 and 16.47 dyn/cm, respectively.

MODIFIED MACLEOD-SUGDEN CORRELATION. With Eq. (12-5.3)

$$\sigma_m^{1/4} = \frac{0.7996}{76.426}\left[\frac{(0.423)(16.47)^{1/4}}{0.7069/74.123} + \frac{(0.577)(28.23)^{1/4}}{0.8722/78.114}\right]$$

$$\sigma_m = 22.63 \text{ dyn/cm}$$

$$\text{Error} = \frac{22.63 - 21.81}{21.81} \times 100 = 3.8\%$$

Although Eq. (12.5-3) yields the correct pure component values of σ, it invariably yields larger errors for σ_m than Eq. (12-5.1).

CORRESPONDING STATES CORRELATION With Eqs. (12-3.6) and (12-3.7) applied to mixtures, assume, for simplicity, mole fraction averages for P_{cm}, T_{cm}, and Q_m:

$$P_{cm} = (0.423)(36.4) + (0.577)(48.9) = 43.6 \text{ bar}$$
$$T_{cm} = (0.423)(466.7) + (0.577)(562.2) = 522 \text{ K}$$

With Q (diethyl ether) $= 0.674$ and Q (benzene) $= 0.628$, we have

$$Q_m = (0.423)(0.674) + (0.577)(0.628) = 0.647$$

Then, with $T_{r_m} = (298)/522 = 0.571$, we get

$$\sigma_m = (43.6)^{2/3}(522)^{1/3}(0.647)(1 - 0.571)^{11/9}$$

$$= 22.97 \text{ dyn/cm}$$

$$\text{Error} = \frac{22.97 - 21.81}{21.81} \times 100 = 5.3\%$$

POWER RELATION.   With Eq. (12-5.2), various values of r can be selected. The results shown below indicate the errors.

r	Calculated σ_m, dyn/cm	% error
1	23.25	6.6
0†	22.48	3.1
−1	21.68	−0.6
−2	20.92	−4.0
−3	20.19	−7.4

†When $q = 0$, $\sigma_m = \sigma_1 \exp[x_2 \ln(\sigma_2/\sigma_1)]$.

Thermodynamic correlations

The estimation procedures introduced earlier in this section are empirical; all employ the bulk liquid (and sometimes vapor) composition to characterize a mixture. However, the "surface phase" differs in composition from that of the bulk liquid and vapor, and it is reasonable to suppose that, in mixture surface tension relations, surface compositions play a more important role than bulk compositions. The fact that σ_m is almost always less than the bulk mole fraction average is interpreted as indicating that the component or components with the lower pure component values of σ preferentially concentrate in the surface phase. Eberhart [14] assumes that σ_m is given by the surface composition–mole fraction average.

Both classical and statistical thermodynamics have been employed to derive expressions for σ_m [5, 11, 15, 16, 28, 29, 30, 34, 59, 60, 62, 65, 69, 76]; the results differ in some aspects, but most arrive at a result similar to

$$\sum_{i=1}^{n} \left(\frac{x_i^B \gamma_i^B}{\gamma_i^\sigma} \right) \exp \frac{\mathcal{A}_i(\sigma_m - \sigma_i)}{RT} = 1 \tag{12-5.4}$$

where x_i^B = mole fraction of i in bulk liquid
γ_i^B = activity coefficient of i in bulk liquid normalized so that $\gamma_i^B \to 1$ as $x_i \to 1$

γ_i^s = activity coefficient of i in surface phase normalized so that $\gamma_i^s \to 1$ as surface phase becomes identical with that for pure i

$\mathcal{A}_i$ = partial molar surface area of i, cm^2/mol

σ_m, σ_i = surface tension of mixture and of component i

The activity coefficients γ_i^B are usually obtained from vapor-liquid equilibrium data or from some liquid model, as discussed in Chap. 8. For the surface phase, however, no direct measurements appear possible, and a liquid model must be assumed. Hildebrand and Scott [29] treat the case of a "perfect" surface phase, $\gamma_i^s = 1$, whereas Eckert and Prausnitz [15] and Sprow and Prausnitz [65] have used regular solution theory to describe the same phase. In all cases, the partial molal area $\mathcal{A}_i$ has been approximated as $(V_i)^{2/3}(N_0)^{1/3}$, where V_i is the *pure liquid* molal volume of i and N_0 is Avogadro's number. Sprow and Prausnitz have successfully applied Eq. (12-5.4) to a variety of nonpolar binary systems and have estimated σ_m accurately. Even for polar mixtures, some success was achieved, although in this case a modified Wilson activity coefficient expression was introduced for the surface phase and one empirical constant was retained to give a good fit between experimental and calculated values of σ_m.

Although the Sprow-Prausnitz approach is more realistic, it is not uncommon to find Eq. (12-5.4) simplified by assuming an ideal-liquid mixture, that is, $\gamma_i^B = \gamma_i^s = 1$. For a binary system, it can then be shown that this equation simplifies to

$$\sigma_m = x_A \sigma_A + x_B \sigma_B - \frac{\mathcal{A}}{2RT}(\sigma_A - \sigma_B)^2 x_A x_B \qquad (12\text{-}5.5)$$

where the terms are as defined above (with x_A, x_B bulk mole fractions) and $\mathcal{A}$ is an average surface area for the molecules constituting the system. This simplified form clearly indicates that σ_m is less than a mole fraction average.

Example 12-4 Repeat Example 12-3 by using the simplified (ideal) form of the thermodynamic correlation.

solution Let subscript A stand for diethyl ether and subscript B for benzene. Then $x_A = 0.423$, $\sigma_A = 16.47$, $x_B = 0.577$, and $\sigma_B = 28.23$, giving

$$RT = (8.314 \times 10^7)(298) = 2.478 \times 10^{10} \text{ ergs/mol K}$$

$$\mathcal{A}_A = \left(\frac{74.123}{0.7069}\right)^{2/3}(6.023 \times 10^{23})^{1/3}$$

$$= 1.775 \times 10^9 \text{ cm}^2/\text{mol}$$

$$\mathcal{A}_B = \left(\frac{78.114}{0.8722}\right)^{2/3}(6.023 \times 10^{23})^{1/3}$$

$$= 1.690 \times 10^9 \text{ cm}^2/\text{mol}$$

With $\mathcal{A} \approx (\mathcal{A}_A + \mathcal{A}_B)/2 = 1.743 \times 10^9$ cm^2/mol, with Eq. (12-5.5) we have

$$\sigma_m = (0.423)(16.47) + (0.577)(28.23)$$
$$- \frac{1.783 \times 10^9}{(2)(2.478 \times 10^{10})} \times (16.47 - 28.23)^2 (0.423)(0.577)$$
$$= 22.03 \text{ dyn/cm}$$
$$\text{Error} = \frac{22.03 - 21.81}{21.81} \times 100 = 1\%$$

Although Example 12-4 shows but a small error when Eq. (12-5.5) is applied to the diethyl ether–benzene system at 298 K, this is more fortuitous than representative. The more accurate form, Eq. (12-5.4), is preferable, though considerably more effort must be expended to utilize it.

Recommendations

For *nonpolar* systems, use Eq. (12-5.4) as prescribed by Sprow and Prausnitz; even polar systems may be treated if at least one mixture value of σ_m is available. Errors are typically less than 2 to 3 percent. For less accurate estimates, there is little choice between the Macleod-Sugden correlation (12-5.1), the corresponding states correlation (12-3.6) (see Example 12-3), and the ideal thermodynamic relation (12-5.5). Errors are generally less than 5 to 10 percent.

For mixtures containing one or more polar components, the corresponding states method cannot be used; also, none of the thermodynamic methods is applicable without introducing a mixture constant. For polar (nonaqueous) systems, therefore, the Macleod-Sugden relation (12-5.1) is the only method available. When employed to correlate the mixture surface tension data of Ling and van Winkle [37], only moderate agreement (5 to 15 percent) was achieved for the polar-polar and polar-nonpolar systems studied.

12-6   Surface Tensions of Aqueous Solutions

Whereas for nonaqueous solutions the mixture surface tension is often approximated by a linear dependence on mole fraction, aqueous solutions show pronounced nonlinear characteristics. A typical case is shown in Fig. 12-5 for acetone-water at 353 K. The surface tension of the mixture is
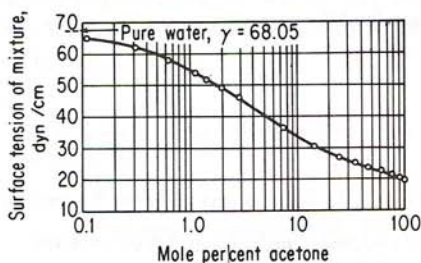
Figure 12-5 Surface tensions of water-acetone solutions at 353 K. *(From Ref. 40.)*

represented by an approximately straight line on semilogarithmic coordinates. This behavior is typical of organic-aqueous systems, in which small concentrations of the organic material may significantly affect the mixture surface tension. The hydrocarbon portion of the organic molecule behaves like a hydrophobic material and tends to be rejected from the water phase by preferentially concentrating on the surface. In such a case, the bulk concentration is very different from the surface concentration. Unfortunately, the latter is not easily amenable to direct measurement. Meissner and Michaels [41] show graphs similar to Fig. 12-5 for a variety of dilute solutions of organic materials in water and suggest that the general behavior is approximated by the Szyszkowski equation, which they modify to the form

$$\frac{\sigma_m}{\sigma_W} = 1 - 0.411 \log\left(1 + \frac{x}{a}\right) \tag{12-6.1}$$

where σ_W = surface tension of pure water
x = mole fraction of organic material
a = constant characteristic of organic material

Values of a are listed in Table 12-2 for a few compounds. This equation should not be used if the mole fraction of the organic solute exceeds 0.01.

The method of Tamura, Kurata, and Odani [70] may be used to estimate surface tensions of aqueous binary mixtures over wide concentration ranges of the dissolved organic material and for both low- and high-molecular weight organic-aqueous systems. Equation (12-5.1) is assumed as a

TABLE 12-2   Constants for the Szyszkowski Equation (12-6.1) [41]

Compound	$a \times 10^4$	Compound	$a \times 10^4$
Propionic acid	26	Ethyl propionate	3.1
n-Propyl alcohol	26	Propyl acetate	3.1
Isopropyl alcohol	26		
Methyl acetate	26	n-Valeric acid	1.7
		Isovaleric acid	1.7
n-Propyl amine	19	n-Amyl alcohol	1.7
Methyl ethyl ketone	19	Isoamyl alcohol	1.7
n-Butyric acid	7.0	Propyl propionate	1.0
Isobutyric acid	7.0	n-Caproic acid	0.75
n-Butyl alcohol	7.0	n-Heptanoic acid	0.17
Isobutyl alcohol	7.0	n-Octanoic acid	0.034
		n-Decanoic acid	0.0025
Propyl formate	8.5		
Ethyl acetate	8.5		
Methyl propionate	8.5		
Diethyl ketone	8.5		

starting point, but the significant densities and concentrations are taken to be those characteristic of the surface layer, that is, $(V^\sigma)^{-1}$ replaces ρ_{Lm}, where V^σ is a hypothetical molal volume of the surface layer. V^σ is estimated with

$$V^\sigma = \sum_j x_j^\sigma V_j \tag{12-6.2}$$

where x_j^σ is the mole fraction of j in the surface layer. V_j, however, is chosen as the pure liquid molal volume of j. Then, with Eq. (12-5.1), assuming $\rho_L \gg \rho_v$,

$$V^\sigma \sigma_m^{1/4} = x_W^\sigma [P_W] + x_O^\sigma [P_O] \tag{12-6.3}$$

where the subscripts W and O represent water and the organic component. To eliminate the parachor, however, Tamura et al. introduce Eq. (12-3.1); the result is

$$\sigma_m^{1/4} = \psi_W^\sigma \sigma_W^{1/4} + \psi_O^\sigma \sigma_O^{1/4} \tag{12-6.4}$$

In Eq. (12-6.4), ψ_W^σ is the superficial volume fraction water in the surface layer

$$\psi_W^\sigma = \frac{x_W^\sigma V_W}{V^\sigma} \tag{12-6.5}$$

and similarly for ψ_O^σ.

Equation (12-6.4) is the final correlation. To obtain values of the superficial surface volume fractions ψ_W^σ and ψ_O^σ, equilibrium is assumed between the surface and bulk phases. Tamura's equation is complex, and after rearrangement it can be written in the following set of equations:

$$\mathcal{B} = \log \frac{\psi_W^q}{\psi_O} \tag{12-6.6}$$

$$\mathcal{C} = \log \frac{(\psi_W^\sigma)^q}{\psi_O^\sigma} \tag{12-6.7}$$

$$\mathcal{C} = \mathcal{B} + \mathcal{W} \tag{12-6.8}$$

$$\mathcal{W} = 0.441 \frac{q}{T} \left(\frac{\sigma_O V_O^{2/3}}{q} - \sigma_W V_W^{2/3} \right) \tag{12-6.9}$$

where ψ_W^σ is defined by Eq. (12-6.5) and ψ_W, ψ_O are the superficial bulk volume fractions of water and organic material, i.e.,

Materials	q	Example
Fatty acids, alcohols	Number of carbon atoms	Acetic acids, $q = 2$
Ketones	One less than the number of carbon atoms	Acetone, $q = 2$
Halogen derivatives of fatty acids	Number of carbons times ratio of molal volume of halogen derivative to parent fatty acid	Chloroacetic acid, $q = 2 \dfrac{V_b \text{ (chloroacetic acid)}}{V_b \text{ (acetic acid)}}$

$$\psi_W = \frac{x_W V_W}{x_W V_W + x_O V_O} \qquad \psi_O = \frac{x_O V_O}{x_W V_W + x_O V_O} \qquad (12\text{-}6.10)$$

where x_W, x_O = bulk mole fraction of pure water and pure organic component

V_W, V_O = molal volume of pure water and pure organic component

σ_W, σ_O = surface tension of pure water and pure organic component

T = temperature, K

q = constant depending upon type and size of organic constituent

The method is illustrated in Example 12-5. Tamura et al. [70] tested the method with some 14 aqueous systems and 2 alcohol-alcohol systems;† the percentage errors are less than 10 percent when q is less than 5 and within 20 percent for q greater than 5. The method cannot be applied to multicomponent mixtures.

Example 12-5 Estimate the surface tension of a mixture of methyl alcohol and water at 303K when the mole fraction alcohol is 0.122. The experimental value reported is 46.1 dyn/cm [70].

solution At 303 K (O represents methyl alcohol, W water), σ_W = 71.18 dyn/cm, σ_O = 21.75 dyn/cm, V_W = 18 cm³/mol, V_O = 41 cm³/mol, and q = number of carbon atoms = 1. From Eqs. (12-6.10),

$$\frac{\psi_W}{\psi_O} = \frac{(0.878)(18)}{(0.122)(41)} = 3.16$$

and from Eq. (12-6.6),

$$\mathcal{B} = \log 3.16 = 0.50$$

$$\mathcal{W} \text{ [from Eq. (12-6.9)]} = (0.441)(\tfrac{1}{303})[(21.75)(41)^{2/3} - (71.18)(18)^{2/3}]$$

$$= -0.34$$

---

†For nonaqueous mixtures comprising polar molecules, the method is unchanged except that q = ratio of molal volumes of the solute to solvent.

Hence

$$\mathcal{C} \text{ [from Eq. (12-6.8)]} = \mathcal{B} + \mathcal{W} = 0.50 - 0.34 = 0.16$$

$$= \log \frac{\psi_W^s}{\psi_0^s} \quad \text{from Eq. (12-6.7)}$$

Since $\psi_W^s + \psi_0^s = 1$, we have

$$\frac{\psi_W^s}{1 - \psi_W^s} = 10^{0.16} = 1.45$$

$$\psi_W^s = 0.59 \qquad \psi_0^s = 0.41$$

Finally, from Eq. (12-6.4)

$$\sigma_m = [(0.59)(71.18)^{1/4} + (0.41)(21.75)^{1/4}]^4 = 46 \text{ dyn/cm}$$

$$\text{Error} = \frac{46 - 46.1}{46.1} \times 100 = -0.2\%$$

Recommendations

For estimating the surface tensions of binary organic-aqueous mixtures, use the method of Tamura, Kurata, and Odani, as given by Eqs. (12-6.2) to (12-6.10) and illustrated in Example 12-5. The method may also be used for other highly polar solutes such as alcohols. Errors normally do not exceed 10 to 15 percent. If the solubility of the organic compound in water is low, the Szyszkowski equation (12-6.1), as developed by Meissner and Michaels, may be used.

Notation

a parameter in Eq. (12-6.1) and obtained from Table 12-2

A area

$\mathcal{A}$ surface area; $\mathcal{A}_i$, partial molal area of component i on the surface

$\mathcal{B}$ parameter in Eq. (12-6.6)

$\mathcal{C}$ parameter in Eq. (12-6.7)

m parameter in Eq. (12-3.8)

n parameter in Eq. (12-3.2)

N_0 Avogadro's number

p parameter in Eq. (12-3.10)

$[P_i]$ parachor of component i (see Table 11-3)

P_{vp} vapor pressure, bar

P_c critical pressure, bar; P_{c_m}, pseudocritical pressure

q parameter in Eq. (12-6.9)

Q parameter in Eq. (12-3.7)

Q_p parameter in Eq. (12-3.8)

r parameter in Eq. (12-5.2)

R gas constant

T temperature, K; T_c, critical temperature; T_b, normal boiling point, T_r, reduced temperature T/T_c; T_{br}, T_b/T_c; T_{cm}, pseudocritical mixture temperature

V liquid molal volume, cm^3/mol; V^σ, for the surface phase

V_c critical volume, cm^3/mol

$\mathcal{W}$ parameter in Eq. (12-6.9)

x_i liquid mole fraction; x_i^B, in the bulk phase; x_i^σ, in the surface phase

y_i vapor mole fraction

GREEK

α_c Riedel factor

γ_i activity coefficient of component i; γ_i^B, in the bulk liquid phase; γ_i^σ, in the surface phase

η liquid or vapor viscosity, cP

ρ liquid or vapor density, mol/cm^3

σ surface tension, dyn/cm; σ_m, for a mixture; σ_O, a parameter in Eq. (12-3.10) or representing an organic component

ψ_i volume fraction of i in the bulk liquid; ψ_i^σ, in the surface phase

SUBSCRIPTS

b normal boiling point

L liquid

m mixture

O   organic component in aqueous solution

r reduced value, i.e., the property divided by its value at the critical point

v vapor

W   water

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Appendix

A

Property Data Bank

The listing of compounds is by the total carbon number. Within each carbon number class, subgroups are indexed by the number of hydrogens and, further, by additional atoms in alphabetical order.

The symbols and equations used are shown below. The enthalpy and Gibbs energy of formation at 298.2 K (DELHF and DELGF) are for the *ideal-gas state*. The reference states chosen for the elements are as follows:

Ideal gases at one atmosphere: Ar, Cl_2, D_2, F_2, He, H_2, Kr, Ne, O_2, Rn, T_2, and Xe. Al (crystal); As (crystal); B (crystal); Br_2 (liquid); C (graphite); Hg (liquid); I_2 (crystal); P (solid, red); S (crystal, rhombic); Se (crystal); Si (crystal); Ti (crystal, alpha); U (crystal).

MolWt = molecular weight, g/mol
Tfp = normal freezing point, K
Tb = normal boiling point (at 1 atm), K
Tc = critical temperature, K
Pc = critical pressure, bar
Vc = critical volume, cm^3/mole
Zc = critical compressibility factor, PcVc/RTc
Omega = Pitzer's acentric factor
Dipm = dipole moment, debyes

CPVAP A, CPVAP B, CPVAP C, CPVAP D = constants to calculate the isobaric heat capacity of the ideal gas, with Cp in J/(mol·K) and T in kelvins:

$$Cp = CPVAP\ A + (CPVAP\ B)T + (CPVAP\ C)T^2 + (CPVAP\ D)T^3$$

DELHF = standard enthalpy of formation for the ideal gas at 298.2 K, J/ mol
(See note above on reference states.)

DELGF = standard Gibbs energy of formation for the ideal gas at 298.2 K and 1 atm, J/ mol
(See note above on reference states.)

Vapor pressure: Pvp = vapor pressure, in bars
Pc = critical pressure, in bars
Tc = critical temperature, in kelvins
T = temperature, in kelvins

There is a choice of equations as noted in the tables:

Equation (1):
$$\ln (Pvp/Pc) = (1 - x)^{-1}[(VP\ A)x + (VP\ B)x^{1.5} + (VP\ C)x^3 + (VP\ D)x^6]$$
$$x = 1 - T/Tc$$
Equation (2):
$$\ln Pvp = VP\ A - (VP\ B)/T + (VP\ C) \ln T + (VP\ D)(Pvp)/T^2$$
Equation (3):
$$\ln Pvp = VP\ A - (VP\ B)/[T + (VP\ C)]$$
LDEN = liquid density, g/cm³
TDEN = temperature for LDEN, K

No	Formula	Name	MolWt	Tfp K	Tb K	Tc K	Pc bar	Vc cm³/mole	Zc	Omega	Dipm debye
1	AlBr3	aluminum tribromide	266.694	370.7	528.	763.	28.9	310.	0.141	0.399	5.0
2	AlCl3	aluminum trichloride	133.341	467.	453.	620.	26.3	259.	0.132	0.660	2.0
3	AlI3	aluminum triiodide	407.697	464.	655.	983.		408.			2.3
4	Ar	argon	39.948	83.8	87.3	150.8	48.7	74.9	0.291	0.001	0.0
5	As	arsenic	74.922		888.	1673.	223.	34.9	0.056	0.121	0.0
6	AsCl3	arsenic trichloride	181.281	264.7	403.	654.		252.			1.6
7	BBr3	boron tribromide	250.568	227.	364.	581.		272.			0.0
8	BCl3	boron trichloride	117.191	165.9	285.8	455.	38.7	239.5	0.245	0.140	0.0
9	BF3	boron trifluoride	67.805	146.5	172.	260.8	49.9	114.7	0.264	0.393	0.0
10	BI3	boron triiodide	391.55	323.1	483.	773.		356.			0.0
11	Br2	bromine	159.808	266.0	331.9	588.	103.	127.2	0.268	0.108	0.2
12	BrI	iodine bromide	206.813	315.	389.	719.		139.			1.2
13	Br3P	phosphorus tribromide	270.723	233.	446.1	711.		300.			0.5
14	Br4Si	silicon tetrabromide	347.702	278.6	427.	663.		382.			0.0
15	Br4Ti	titanium tetrabromide	367.536	312.	503.	795.7		391.			
16	ClFO3	perchloryl fluoride	102.448	125.5	226.4	368.4	53.7	160.8	0.282	0.170	0.0
17	ClF2N	nitrogen chloride difluoride	87.456		207.	337.5	51.5			0.154	
18	ClF2P	phosphorus chloride difluoride	104.423		225.9	362.4	45.2			0.164	
19	ClF2PS	thiophosphoryl chloride difluoride	136.489		279.	439.2	41.4			0.202	
20	ClF5	chlorine pentafluoride	130.443		260.0	416.	52.7	233.	0.355	0.216	
21	ClNO	nitrosyl chloride	65.459	213.5	267.7	440.	79.8	123.8	0.285	0.090	1.8
22	Cl2	chlorine	70.906	172.2	239.2	416.9	49.6			0.174	0.0
23	Cl2FP	phosphorus dichloride fluoride	120.878		287.0	463.0		264.			0.9
24	Cl3P	phosphorus trichloride	137.333	161.	349.1	563.	35.9			0.232	0.0
25	Cl4Si	silicon tetrachloride	169.898	204.3	330.8	508.1		325.7	0.277		

No	Formula	Name	CPVAP A	CPVAP B	CPVAP C	CPVAP D	DELHF	DELGF
1	AlBr3	aluminum tribromide	6.494E+1	6.098E-2	-7.306E-5	2.978E-8	-4.233E+5	-4.522E+5
2	AlCl3	aluminum trichloride	5.054E+1	1.037E-1	-1.202E-4	4.793E-8	-5.849E+5	-5.704E+5
3	AlI3	aluminum triiodide	6.270E+1	6.802E-2	-8.113E-5	3.298E-8	-2.052E+5	-2.531E+5
4	Ar	argon	2.080E+1				0.0	0.0
5	As	arsenic						
6	AsCl3	arsenic trichloride						
7	BBr3	boron tribromide	4.331E+1	1.160E-1	-1.267E-4	4.849E-8	-2.043E+5	-2.312E+5
8	BCl3	boron trichloride	3.261E+1	1.390E-1	-1.461E-4	5.439E-8	-4.032E+5	-3.882E+5
9	BF3	boron trifluoride	1.858E+1	1.399E-1	-1.217E-4	3.916E-8	-1.136E+6	-1.120E+6
10	BI3	boron triiodide	4.937E+1	1.028E-1	-1.159E-4	4.529E-8	7.118E+4	2.089E+4
11	Br2	bromine	3.386E+1	1.125E-2	-1.192E-5	4.534E-9	3.093E+4	3.136E+3
12	BrI	iodine bromide	3.402E+1	1.229E-2	-1.420E-5	5.847E-9	4.091E+4	3.714E+3
13	Br3P	phosphorus tribromide	6.102E+1	7.421E-2	-8.899E-5	3.631E-8	-1.285E+5	-1.575E+5
14	Br4Si	silicon tetrabromide	7.466E+1	1.097E-1	-1.298E-4	5.246E-8	-4.159E+5	-4.324E+5
15	Br4Ti	titanium tetrabromide	8.499E+1	7.785E-2	-9.361E-5	3.826E-8	-5.506E+5	-5.695E+5
16	ClFO3	perchloryl fluoride	1.245E+1	2.390E-1	-2.346E-4	8.321E-8	-2.144E+4	5.062E+4
17	ClF2N	nitrogen chloride difluoride						
18	ClF2P	phosphorus chloride difluoride						
19	ClF2PS	thiophosphoryl chloride difluoride						
20	ClF5	chlorine pentafluoride	3.098E+1	3.203E-1	-3.685E-4	1.462E-7	-2.386E+5	-1.469E+5
21	ClNO	nitrosyl chloride	3.410E+1	4.472E-2	-3.340E-5	1.015E-8	5.263E+4	6.699E+4
22	Cl2	chlorine	2.693E+1	3.384E-2	-3.869E-5	1.547E-8	0.0	0.0
23	Cl2FP	phosphorus dichloride fluoride						
24	Cl3P	phosphorus trichloride	4.849E+1	1.131E-1	-1.334E-4	5.380E-8	-2.713E+5	-2.577E+5
25	Cl4Si	silicon tetrachloride	5.658E+1	1.636E-1	-1.897E-4	7.565E-8	-6.577E+5	-6.178E+5

No	Formula	Name	Eq.	VP A	VP B	VP C	VP D	Tmin	Tmax	LDEN	TDEN
1	AlBr3	aluminum tribromide									
2	AlCl3	aluminum trichloride									
3	AlI3	aluminum triiodide								1.31	473
4	Ar	argon	1	-5.90501	1.12627	-0.76787	-1.62721	84	TC	1.373	90
5	As	arsenic									
6	AsCl3	arsenic trichloride								2.163	293
7	BBr3	boron tribromide								2.643	291
8	BCl3	boron trichloride	2	46.103	4443.16	-5.404	2228.	230	TC	1.349	284
9	BF3	boron trifluoride	2	61.138	3481.19	-7.963	576.	160	TC	2.811	293
10	BI3	boron triiodide								3.35	323
11	Br2	bromine	3	9.2239	2582.32	-51.56		259	354	3.119	293
12	BrI	iodine bromide									
13	Br3P	phosphorous tribromide								2.852	288
14	Br4Si	silicon tetrabromide								2.772	298
15	Br4Ti	titanium tetrabromide									
16	ClFO3	perchloryl fluoride									
17	ClF2N	nitrogen chloride difluoride									
18	ClF2P	phosphorous chloride difluoride									
19	ClF2PS	thiophosphoryl chloride difluoride									
20	ClF5	chlorine pentafluoride								2.003	399
21	ClNO	nitrosyl chloride	2	29.760	3748.59	-2.819	900.	230	TC	1.42	261
22	Cl2	chlorine	1	-6.34074	1.15037	-1.40416	-2.23220	206	TC	1.563	239
23	Cl2FP	phosphorous dichloride fluoride									
24	Cl3P	phosphorus trichloride								1.574	294
25	Cl4Si	silicon tetrachloride	3	9.1817	2634.16	-43.15		238	364	1.48	293

No	Formula	Name	MolWt	Tfp K	Tb K	Tc K	Pc bar	Vc cm³/mol	Zc	Omega	Dipm debye
26	C14Ti	titanium tetrachloride	189.712	243.	409.6	638.	46.6	339.2	0.298	0.268	0.0
27	C15P	phosphorus pentachloride	208.260	148.	433.	646.					0.8
28	D2	deuterium (equilibrium)	4.032	18.7	23.6	38.2	16.5	60.3	0.313	-0.137	0.0
29	D2	deuterium (normal)	4.032	18.6	23.5	38.4	16.6			-0.160	0.0
30	D2O	deuterium oxide	20.031	277.0	374.6	644.0	216.6	56.6	0.225	0.351	1.9
31	FNO2	nitryl fluoride	65.003		213.2	349.5					0.5
32	F2	fluorine	37.997	53.5	85.0	144.3	52.2	66.3	0.288	0.054	0.0
33	F2N2	cis-difluorodiazine	66.010		167.5	272.	70.9			0.252	
34	F2N2	trans-difluorodiazine	66.010		161.7	260.	55.7			0.217	
35	F2O	oxygen difluoride	53.995	50.	128.4	215.	49.6				0.2
36	F2Xe	xenon difluoride	169.296		387.5	631.	93.2	148.6	0.264	0.317	
37	F3N	nitrogen trifluoride	71.002	66.4	144.4	234.0	45.3			0.135	0.2
38	F3NO	trifluoroamine oxide	87.001		186.	303.	64.3	146.9	0.375	0.212	
39	F3P	phosphorus trifluoride	87.968		178.	271.2	43.3			0.326	
40	F3PS	thiophosphoryl trifluoride	120.034		220.9	346.0	38.2			0.187	0.6
41	F4N2	tetrafluorohydrazine	104.016	105.	199.	309.	37.5			0.206	0.3
42	F4S	sulfur tetrafluoride	108.058	152.	232.7	364.					1.0
43	F4Si	silicon tetrafluoride	104.09	183.0	187.	259.0	37.2			0.753	0.0
44	F4Xe	xenon tetrafluoride	207.292	387.	388.9	612.	70.4	188.6	0.261	0.357	
45	F6S	sulfur hexafluoride	146.054	222.5	209.6	318.7	37.6	198.8	0.282	0.286	0.0
46	F6U	uranium hexafluoride	352.018	337.	329.	505.8	46.6	250.0	0.277	0.318	0.0
47	He	helium-3	3.017		3.19	3.31	1.14	72.9	0.302	-0.473	0.0
48	He	helium-4	4.003		4.25	5.19	2.27	57.4	0.302	-0.365	0.0
49	Hg	mercury	200.61	234.3	630.	1765.	1510.	42.7	0.439	-0.167	
50	I2	iodine	253.82	386.8	457.5	819.		155.			1.3

No	Formula	Name	CPVAP A	CPVAP B	CPVAP C	CPVAP D	DELHF	DELGF
26	Cl4Ti	titanium tetrachloride	7.064E+1	1.224E-1	-1.443E-4	5.819E-8	-7.637E+5	-7.272E+5
27	Cl5P	phosphorus pentachloride	6.946E+1	2.079E-1	-2.455E-4	9.914E-8	-3.429E+5	-2.785E+5
28	D2	deuterium (equilibrium)	3.025E+1	-6.615E-3	1.170E-5	-3.684E-9	0.0	0.0
29	D2	deuterium (normal)					0.0	0.0
30	D2O	deuterium oxide	3.182E+1	3.045E-3	2.033E-5	-9.737E-9	-2.494E+5	-2.348E+5
31	FNO2	nitryl fluoride	1.778E+1	1.416E-1	-1.254E-4	4.140E-8	-1.089E+5	-6.649E+4
32	F2	fluorine	2.322E+1	3.657E-2	-3.613E-5	1.204E-8	0.0	0.0
33	F2N2	cis-difluorodiazine	1.121E+1	1.754E-1	-1.688E-4	5.898E-8	6.866E+4	1.088E+5
34	F2N2	trans-difluorodiazine	2.254E+1	1.377E-1	-1.258E-4	4.232E-8	8.122E+4	1.205E+5
35	F2O	oxygen difluoride	2.207E+1	9.875E-2	-1.028E-4	3.796E-8	2.453E+4	4.178E+4
36	F2Xe	xenon difluoride						
37	F3N	nitrogen trifluoride	1.141E+1	1.948E-1	-2.023E-4	7.454E-8	-1.316E+5	-9.010E+4
38	F3NO	trifluoroamine oxide	1.513E+1	2.446E-1	-2.528E-4	9.375E-8	-1.633E+5	-9.646E+4
39	F3P	phosphorus trifluoride	2.179E+1	1.733E-1	-1.852E-4	6.974E-8	-9.378E+5	-9.253E+5
40	F3PS	thiophosphoryl trifluoride	2.492E+1	2.326E-1	-2.472E-4	9.275E-8	-9.923E+5	-9.743E+5
41	F4N2	tetrafluorohydrazine	3.553E+0	3.509E-1	-3.637E-4	1.338E-7	-8.374E+3	7.988E+4
42	F4S	sulfur tetrafluoride	2.542E+1	2.420E-1	-2.653E-4	1.017E-7	-7.813E+5	-7.406E+5
43	F4Si	silicon tetrafluoride	2.678E+1	2.157E-1	-2.204E-4	8.031E-8	-1.616E+6	-1.574E+6
44	F4Xe	xenon tetrafluoride					-1.876E+6	
45	F6S	sulfur hexafluoride	-6.599E-1	4.639E-1	-5.089E-4	1.953E-7	-1.222E+6	-1.118E+6
46	F6U	uranium hexafluoride					-2.139E+6	-2.060E+6
47	He	helium-3	2.080E+1				0.0	0.0
48	He	helium-4	2.080E+1				0.0	0.0
49	Hg	mercury	2.080E+1				6.134E+4	3.186E+4
50	I2	iodine	3.559E+1	6.515E-3	-6.988E-6	2.834E-9	6.247E+4	1.938E+4

No	Formula	Name	Eq.	VP A	VP B	VP C	VP D	Tmin	Tmax	LDEN	TDEN
26	C14Ti	titanium tetrachloride									
27	C15P	phosphorous pentachloride								1.70	298
28	D2	deuterium (equilibrium)	3	6.6752	157.89	0.0		19	25	0.165	22.7
29	D2	deuterium (normal)									
30	D2O	deuterium oxide								1.105	298
31	FNO2	nitryl fluoride									
32	F2	fluorine	1	-6.18224	1.18062	-1.16555	-1.50167	64	TC	1.51	85
33	F2N2	cis-difluorodiazine									
34	F2N2	trans-difluorodiazine									
35	F2O	oxygen difluoride								1.521	128
36	F2Xe	xenon difluoride									
37	F3N	nitrogen trifluoride	2	32.599	1970.37	-3.81	509.	130	TC	1.54	144
38	F3NO	fluoroamine oxide									
39	F3P	phosphorous trifluoride								3.1	172
40	F3PS	thiophosphoryl trifluoride									
41	F4N2	tetrafluorohydrazine									
42	F4S	sulfur tetrafluoride	3	7.4561	1218.59	-73.24		161	224	1.5	163
43	F4Si	silicon tetrafluoride								1.936	195
44	F4Xe	xenon tetrafluoride									
45	F6S	sulfur hexafluoride	-3	12.7583	2524.78	-11.16		159	220	1.83	223
46	F6U	uranium hexafluoride									
47	He	helium-3									
48	He	helium-4	1	-3.97466	1.00074	1.50056	-0.43020	2	TC	0.123	4.3
49	Hg	mercury								13.594	293
50	I2	iodine	3	9.5395	3709.23	-68.16		383	487	3.74	453

No	Formula	Name	MolWt	Tfp K	Tb K	Tc K	Pc bar	Vc cm^3/mol	Zc	Omega	Dipm debye
51	I4Si	silicon tetraiodide	535.706	393.7	560.5	944.		558.			
52	I4Ti	titanium tetraiodide	555.520	423.	650.	1040.		505.			
53	Kr	krypton	83.800	115.8	119.9	209.4	55.0	91.2	0.288	0.005	0.0
54	NO	nitric oxide	30.006	109.5	121.4	180.	64.8	57.7	0.250	0.588	0.2
55	NO2	nitrogen dioxide	46.006	261.9	294.3	431.	101.	167.8	0.473	0.834	0.4
56	N2	nitrogen	28.013	63.3	77.4	126.2	33.9	89.8	0.290	0.039	0.0
57	N2O	nitrous oxide	44.013	182.3	184.7	309.6	72.4	97.4	0.274	0.165	0.2
58	Ne	neon	20.183	24.5	27.1	44.4	27.6	41.6	0.311	-0.029	0.0
59	O2	oxygen	31.999	54.4	90.2	154.6	50.4	73.4	0.288	0.025	0.0
60	O2S	sulfur dioxide	64.063	197.7	263.2	430.8	78.8	122.2	0.269	0.256	1.6
61	O3	ozone	47.998	80.5	181.2	261.1	55.7	88.9	0.228	0.691	0.6
62	O3S	sulfur trioxide	80.058	290.	318.	491.0	82.1	127.3	0.256	0.481	0.0
63	P	phosphorous	30.974		553.	994.					
64	Rn	radon	222.00	202.	211.4	377.	62.8			-0.008	
65	S	sulfur	32.066		717.8	1314.	207.			0.171	
66	Se	selenium	78.96		1010.	1766.	272.	58.	0.287	0.346	0.0
67	T2	tritium	6.32		25.0	40.0					
68	Xe	xenon	131.300	161.3	165.0	289.7	58.4	118.4		0.008	0.0
69	HBr	hydrogen bromide	80.912	187.1	206.8	363.2	85.5			0.088	0.8
70	HCl	hydrogen chloride	36.461	159.0	188.1	324.7	83.1	80.9	0.249	0.133	1.1
71	HD	hydrogen deuteride	3.023	16.6	22.1	36.0	14.8	62.7	0.310	-0.179	0.0
72	HF	hydrogen fluoride	20.006	190.	293.	461.	64.8	69.2	0.117	0.329	1.9
73	HI	hydrogen iodide	127.912	222.4	237.6	424.0	83.1			0.049	0.5
74	HF2N	difluoroamine	53.011		250.	403.					
75	H2	hydrogen (equilibrium)	2.016	14.0	20.3	33.0	12.9	64.3	0.303	-0.216	0.0

No	Formula	Name	CPVAP A	CPVAP B	CPVAP C	CPVAP D	DELHF	DELGF
51	I4Si	silicon tetraiodide	8.479E+1	7.800E-2	-9.340E-5	3.806E-8	-1.105E+5	-1.598E+5
52	I4Ti	titanium tetraiodide	9.575E+1	4.253E-2	-5.179E-5	2.135E-8	-2.775E+5	-3.282E+5
53	Kr	krypton	2.080E+1				0.0	0.0
54	NO	nitric oxide	2.935E+1	-9.378E-4	9.747E-6	-4.187E-9	9.043E+4	8.675E+4
55	NO2	nitrogen dioxide	2.423E+1	4.836E-2	-2.081E-5	0.293E-9	3.387E+4	5.200E+4
56	N2	nitrogen	3.115E+1	-1.357E-2	2.680E-5	-1.168E-8	0.0	0.0
57	N2O	nitrous oxide	2.162E+1	7.281E-2	-5.778E-5	1.830E-8	8.160E+4	1.037E+5
58	Ne	neon	2.080E+1				0.0	0.0
59	O2	oxygen	2.811E+1	-3.680E-6	1.746E-5	-1.065E-8	0.0	0.0
60	O2S	sulfur dioxide	2.385E+1	6.699E-2	-4.961E-5	1.328E-8	-2.971E+5	-3.004E+5
61	O3	ozone	2.054E+1	8.009E-2	-6.243E-5	1.697E-8	1.428E+5	1.629E+5
62	O3S	sulfur trioxide	1.921E+1	1.374E-1	-1.176E-4	3.700E-8	-3.960E+5	-3.713E+5
63	P	phosphorous	2.080E+1				3.341E+5	2.922E+5
64	Rn	radon	2.080E+1				0.0	0.0
65	S	sulfur					2.792E+5	2.386E+5
66	Se	selenium						
67	T2	tritium						
68	Xe	xenon	2.080E+1				0.0	0.0
69	HBr	hydrogen bromide	3.065E+1	-9.462E-3	1.722E-5	-6.238E-9	-3.626E+4	-5.330E+4
70	HCl	hydrogen chloride	3.067E+1	-7.201E-3	1.246E-5	-3.898E-9	-9.236E+4	-9.533E+4
71	HD	hydrogen deuteride	2.947E+1	-1.329E-3	1.311E-6	1.279E-9	3.220E+2	-1.465E+3
72	HF	hydrogen fluoride	2.906E+1	6.611E-4	-2.032E-6	2.504E-9	-2.713E+5	-2.734E+5
73	HI	hydrogen iodide	3.116E+1	-1.428E-2	2.972E-5	-1.353E-8	2.638E+4	1.591E+3
74	HF2N	difluoroamine						
75	H2	hydrogen (equilibrium)	2.714E+1	9.274E-3	-1.381E-5	7.645E-9	0.0	0.0

No	Formula	Name	Eq.	VP A	VP B	VP C	VP D	Tmin	Tmax	LDEN	TDEN
51	I4Si	silicon tetraiodide									
52	I4Ti	titanium tetraiodide									
53	Kr	krypton	2	24.097	1408.77	-2.579	336.	115	TC	2.42	120
54	NO	nitric oxide	2	54.894	2465.78	-7.211	209.	115	TC	1.28	121
55	NO2	nitrogen dioxide	2	55.242	6073.34	-6.094	780.	270	TC	1.45	293
56	N2	nitrogen	1	-6.09676	1.13670	-1.04072	-1.93306	63	TC	0.804	78
57	N2O	nitrous oxide	2	39.824	2867.98	-4.655	557.	190	TC	1.226	184
58	Ne	neon	1	-6.07686	1.59402	-1.06092	4.06656	25	TC	1.204	27
59	O2	oxygen	1	-6.28275	1.73619	-1.81349	-2.53645E-2	54	TC	1.149	90
60	O2S	sulfur dioxide	2	48.882	4552.50	-5.666	990.	235	TC	1.455	263
61	O3	ozone	3	9.1225	1272.18	-22.16		109	174	1.356	161
62	O3S	sulfur trioxide	2	132.94	10420.1	-17.38	1200.	300	TC	1.78	318
63	P	phosphorous									
64	Rn	radon								4.4	211
65	S	sulfur									
66	Se	selenium									
67	T2	tritium									
68	Xe	xenon	2	24.809	1951.76	-2.544	603.	170	TC	3.06	165
69	HBr	hydrogen bromide	2	21.482	2394.35	-1.843	653.	200	TC	2.16	216
70	HCl	hydrogen chloride	2	31.994	2626.67	-3.443	538.	180	TC	1.193	188
71	HD	hydrogen deuteride									
72	HF	hydrogen fluoride	1	-9.74369	4.68946	-2.98358	9.65825	273	TC	0.967	293
73	HI	hydrogen iodide	2	27.264	3013.08	-2.673	923.	235	TC	2.80	237
74	HF2N	difluoroamine									
75	H2	hydrogen (equilibrium)	1	-5.57929	2.60012	-0.85506	1.70503	14	TC	0.071	20

No	Formula	Name	MolWt	Tfp K	Tb K	Tc K	Pc bar	Vc cm³/mol	Zc	Omega	Dipm debye
76	H2	hydrogen (normal)	2.016	14.0	20.4	33.2	13.0	65.1	0.306	-0.218	0.0
77	H2O	water	18.015	273.2	373.2	647.3	221.2	57.1	0.235	0.344	1.8
78	H2S	hydrogen sulfide	34.080	189.6	213.5	373.2	89.4	98.6	0.284	0.097	0.9
79	H3As	arsine	77.946	159.7	218.	373.1					0.2
80	H3N	ammonia	17.031	195.4	239.8	405.5	113.5	72.5	0.244	0.250	1.5
81	H3P	phosphine	33.998	140.	185.4	324.5	65.4			0.038	0.6
82	H4ClN	ammonium chloride	53.492		793.	882.	16.4			3.92	
83	H4ClP	phosphonium chloride	70.459		246.	322.3	73.7			1.64	
84	H4N2	hydrazine	32.045	274.7	386.7	653.	147.			0.316	3.0
85	H4Si	silane	32.122	88.2	161.	269.7	48.4			0.068	0.0
86	H6B2	diborane	27.668	108.	185.6	289.8	40.5			0.217	0.0
87	CBrClF2	bromochlorodifluoromethane	165.364		269.	426.9	42.5	245.5	0.294	0.184	
88	CBr2F2	dibromodifluoromethane	209.815	132.	298.	471.3	41.3				
89	CBrF3	trifluorobromomethane	148.910	92.0	215.3	340.2	39.7	195.9	0.275	0.171	0.7
90	CClF3	chlorotrifluoromethane	104.459		193.2	302.0	38.7	180.4	0.278	0.198	0.5
91	CCl2F2	dichlorodifluoromethane	120.914	115.4	245.2	385.0	41.4	216.7	0.280	0.204	0.5
92	CCl2O	phosgene	98.916	145.0	281.	455.	56.7	190.1	0.285	0.205	1.1
93	CCl3F	trichlorofluoromethane	137.368	162.0	296.9	471.2	44.1	247.8	0.279	0.189	0.5
94	CCl4	carbon tetrachloride	153.823	250.	349.9	556.4	45.6	275.9	0.272	0.193	0.0
95	CD4	deuteromethane	20.071		111.7	189.2	46.6	98.2	0.291	0.032	0.0
96	CF4	carbon tetrafluoride	88.005	86.4	145.1	227.6	37.4	139.6	0.276	0.177	0.0
97	CO	carbon monoxide	28.010	68.1	81.7	132.9	35.0	93.2	0.295	0.066	0.1
98	COS	carbonyl sulfide	60.070	134.3	223.	378.8	63.5	136.3	0.275	0.105	0.7
99	CO2	carbon dioxide	44.010	216.6		304.1	73.8	93.9	0.274	0.239	0.0
100	CS2	carbon disulfide	76.131	161.3	319.	552.	79.0	160.	0.276	0.109	0.0

No	Formula	Name	CPVAP A	CPVAP B	CPVAP C	CPVAP D	DELHF	DELGF
76	H2	hydrogen (normal)						
77	H2O	water	3.224E+1	1.924E-3	1.055E-5	-3.596E-9	-2.420E+5	-2.288E+5
78	H2S	hydrogen sulfide	3.194E+1	1.436E-3	2.432E-5	-1.176E-8	-2.018E+4	-3.308E+4
79	H3As	arsine					1.825E+5	1.578E+5
80	H3N	ammonia	2.731E+1	2.383E-2	1.707E-5	-1.185E-8	-4.572E+4	-1.616E+4
81	H3P	phosphine	2.323E+1	4.401E-2	1.303E-5	-1.593E-8	2.290E+4	2.541E+4
82	H4ClN	ammonium chloride						
83	H4ClP	phosphonium chloride						
84	H4N2	hydrazine	9.768E+0	1.895E-1	-1.657E-4	6.025E-8	9.525E+4	1.586E+5
85	H4Si	silane	1.118E+1	1.220E-1	-5.548E-5	6.840E-9	3.266E+4	5.518E+4
86	H6B2	diborane					3.140E+4	8.332E+4
87	CBrClF2	bromochlorodifluoromethane						
88	CBr2F2	dibromodifluoromethane						
89	CBrF3	trifluorobromomethane	2.188E+1	2.159E-1	-2.114E-4	7.464E-8	-6.494E+5	-6.975E+5
90	CClF3	chlorotrifluoromethane	2.281E+1	1.911E-1	-1.576E-4	4.459E-8	-6.950E+5	-6.544E+5
91	CCl2F2	dichlorodifluoromethane	3.160E+1	1.782E-1	-1.509E-4	4.342E-8	-4.815E+5	-4.425E+5
92	CCl2O	phosgene	2.809E+1	1.361E-1	-1.374E-4	5.070E-8	-2.211E+5	-2.069E+5
93	CCl3F	trichlorofluoromethane	4.098E+1	1.668E-1	-1.416E-4	4.146E-8	-2.847E+5	-2.455E+5
94	CCl4	carbon tetrachloride	4.072E+1	2.049E-1	-2.270E-4	8.843E-8	-1.005E+5	-5.828E+4
95	CD4	deuteromethane	1.249E+1	1.010E-1	-2.199E-5	-8.458E-9	-8.830E+4	-5.954E+4
96	CF4	carbon tetrafluoride	1.398E+1	2.026E-1	-1.625E-4	4.513E-8	-9.337E+5	-8.890E+5
97	CO	carbon monoxide	3.087E+1	-1.285E-2	2.789E-5	-1.272E-8	-1.106E+5	-1.374E+5
98	COS	carbonyl sulfide	2.357E+1	7.984E-2	-7.017E-5	2.453E-8	-1.385E+5	-1.658E+5
99	CO2	carbon dioxide	1.980E+1	7.344E-2	-5.602E-5	1.715E-8	-3.938E+5	-3.946E+5
100	CS2	carbon disulfide	2.744E+1	8.127E-2	-7.666E-5	2.673E-8	1.171E+5	6.695E+4

No	Formula	Name	Eq.	VP A	VP B	VP C	VP D	Tmin	Tmax	LDEN	TDEN
76	H2	hydrogen (normal)									
77	H2O	water	1	-7.76451	1.45838	-2.77580	-1.23303	275	TC	0.998	293
78	H2S	hydrogen sulfide	2	36.067	3132.31	-3.985	653.	205	TC	0.993	214
79	H3As	arsine								1.604	209
80	H3N	ammonia	2	45.327	4104.67	-5.146	615.	220	TC	0.639	273
81	H3P	phosphine									
82	H4ClN	ammonium chloride								1.529	298
83	H4ClP	phosphonium chloride									
84	H4N2	hydrazine	2	49.476	6951.84	-5.286	1222.	350	TC	1.008	293
85	H4Si	silane								0.68	88
86	H6B2	diborane	3	8.0390	1200.78	-31.22		118	181	0.470	153
87	CBrClF2	bromochlorodifluoromethane	3	9.1295	2154.39	-32.87		178	283	2.462	288
88	CBr2F2	dibromodifluoromethane	3	9.8485	2720.78	-19.35		247	296	1.538	298
89	CBrF3	trifluorobromomethane									
90	CClF3	chlorotrifluoromethane	1	-6.78845	1.24435	-2.32601	1.45543	233	TC	1.298	243
91	CCl2F2	dichlorodifluoromethane	1	-7.01657	1.73224	-2.97909	-0.37723	155	TC	1.750	158
92	CCl2O	phosgene	1	-7.08177	1.60461	-2.57153	-1.88377	216	TC	1.381	293
93	CCl3F	trichlorofluoromethane	2	42.089	4464.14	-4.753	2138.	260	TC	1.494	290
94	CCl4	carbon tetrachloride	1	-7.07139	1.71497	-2.89930	-2.49466	250	TC	1.584	298
95	CD4	deuteromethane									
96	CF4	carbon tetrafluoride	3	9.4341	1244.55	-13.06		93	148	1.33	193
97	CO	carbon monoxide	1	-6.20798	1.27885	-1.34533	-2.56842	71	TC	0.803	81
98	COS	carbonyl sulfide	1	-6.40952	1.21015	-1.54976	-2.10074	162	TC	1.274	174
99	CO2	carbon dioxide	1	-6.95626	1.19695	-3.12614	2.99448	217	TC		
100	CS2	carbon disulfide	1	-6.63896	1.20395	-0.37653	-4.32820	277	TC	1.293	273

No	Formula	Name	MolWt	Tfp K	Tb K	Tc K	Pc bar	Vc cm³/mol	Zc	Omega	Dipm debye
101	CHClF2	chlorodifluoromethane	86.469	113.	232.4	369.3	49.7	165.6	0.268	0.221	1.4
102	CHCl2F	dichloromonofluoromethane	102.923	138.	282.1	451.6	51.8	196.4	0.271	0.210	1.3
103	CHCl3	chloroform	119.378	209.6	334.3	536.4	53.7	238.9	0.293	0.218	1.1
104	CHF3	fluoroform	70.013	110.	191.0	299.3	48.6	132.7	0.259	0.260	1.6
105	CHN	hydrogen cyanide	27.026	259.9	298.9	456.7	53.9	138.8	0.197	0.388	3.0
106	CH2Br2	dibromomethane	173.835	220.6	370.	583.	71.				1.9
107	CH2Cl2	dichloromethane	84.933	178.1	313.0	510.	63.			0.199	1.8
108	CH2F2	difluoromethane	52.023		221.5	351.6	58.3	120.8	0.241	0.271	2.0
109	CH2O	formaldehyde	30.026	156.	254.	408.	65.9			0.253	2.3
110	CH2O2	formic acid	46.025	281.5	373.8	580.					1.5
111	CH3Br	methyl bromide	94.939	179.5	276.6	464.	66.1	138.9	0.269	0.153	1.8
112	CH3Cl	methyl chloride	50.488	175.4	249.1	416.3	67.0	113.2	0.240	0.187	1.9
113	CH3F	methyl fluoride	34.033	131.4	194.7	315.0	56.				1.8
114	CH3I	methyl iodide	141.939	206.7	315.7	528.	65.9				1.6
115	CH3NO2	nitromethane	61.041	244.6	374.3	588.	63.1	173.2	0.208	0.310	3.1
116	CH4	methane	16.043	90.7	111.6	190.4	46.0	99.2	0.288	0.011	0.0
117	CH4O	methanol	32.042	175.5	337.7	512.6	80.9	118.0	0.224	0.556	1.7
118	CH4S	methyl mercaptan	48.107	150.	279.1	470.0	72.3	144.8	0.268	0.153	1.3
119	CH5N	methyl amine	31.058	179.7	266.8	430.0	74.3			0.292	1.3
120	CH6N2	methyl hydrazine	46.072		362.	567.	82.4	271.2	0.474	0.425	1.7
121	CH6Si	methyl silane	46.145	116.7	215.6	352.5	36.1	368.	0.285	0.248	0.7
122	C2BrClF3	1,2-dibromo-1-chlorotrifluoroethane	276.277	182.7	366.	560.7	33.9	341.	0.285	0.245	
123	C2Br2F4	1,2-dibromotetrafluoroethane	259.822	163.	320.4	487.8					
124	C2ClF3	chlorotrifluoroethene	116.469	116.	245.3	379.	40.5	212.	0.272	0.252	0.4
125	C2ClF5	chloropentafluoroethane	154.467	167.	235.2	353.2	32.3	251.8	0.277	0.279	0.3

No	Formula	Name	CPVAP A	CPVAP B	CPVAP C	CPVAP D	DELHF	DELGF
101	CHClF2	chlorodifluoromethane	1.730E+1	1.618E-1	-1.170E-4	3.058E-8	-5.020E+5	-4.709E+5
102	CHCl2F	dichloromonofluoromethane	2.366E+1	1.581E-1	-1.200E-4	3.264E-8	-2.989E+5	-2.684E+5
103	CHCl3	chloroform	2.400E+1	1.893E-1	-1.841E-4	6.657E-8	-1.013E+5	-6.858E+4
104	CHF3	fluoroform	8.156E+0	1.813E-1	-1.379E-4	3.938E-8	-6.975E+5	-6.628E+5
105	CHN	hydrogen cyanide	2.186E+1	6.062E-2	-4.961E-5	1.815E-8	1.306E+5	1.202E+5
106	CH2Br2	dibromomethane	2.500E+1	2.517E-1	-1.833E-4	5.646E-8	-3.890E+4	-1.059E+4
107	CH2Cl2	dichloromethane	1.295E+1	1.623E-1	-1.302E-4	4.208E-8	-9.546E+4	-6.891E+4
108	CH2F2	difluoromethane	1.179E+1	1.181E-1	-4.843E-5	2.125E-9	-4.509E+5	-4.229E+5
109	CH2O	formaldehyde	2.348E+1	3.157E-2	2.985E-5	-2.300E-8	-1.160E+5	-1.100E+5
110	CH2O2	formic acid	1.171E+1	1.358E-1	-8.411E-5	2.017E-8	-3.789E+5	-3.512E+5
111	CH3Br	methyl bromide	1.443E+1	1.091E-1	-5.401E-5	1.000E-8	-3.768E+4	-2.818E+4
112	CH3Cl	methyl chloride	1.388E+1	1.014E-1	-3.889E-5	2.567E-9	-8.637E+4	-6.293E+4
113	CH3F	methyl fluoride	1.382E+1	8.616E-2	-2.071E-5	-1.985E-9	-2.340E+5	-2.101E+5
114	CH3I	methyl iodide	1.081E+1	1.389E-1	-1.041E-4	3.486E-8	1.398E+4	1.566E+4
115	CH3NO2	nitromethane	7.423E+0	1.978E-1	-1.081E-4	2.085E-8	-7.478E+4	-6.950E+3
116	CH4	methane	1.925E+1	5.213E-2	1.197E-5	-1.132E-8	-7.490E+4	-5.087E+4
117	CH4O	methanol	2.115E+1	7.092E-2	2.587E-5	-2.852E-8	-2.013E+5	-1.626E+5
118	CH4S	methyl mercaptan	1.327E+1	1.457E-1	-8.545E-5	2.075E-8	-2.299E+4	-9.923E+3
119	CH5N	methyl amine	1.148E+1	1.427E-1	-5.334E-5	4.752E-9	-2.303E+4	3.228E+4
120	CH6N2	methyl hydrazine					8.541E+4	1.780E+5
121	CH6Si	methyl silane						
122	C2Br2ClF3	1,2-dibromo-1-chlorotrifluoroethane						
123	C2Br2F4	1,2-dibromotetrafluoroethane						
124	C2ClF3	chlorotrifluoroethene					-7.662E+5	
125	C2ClF5	chloropentafluoroethane	2.783E+1	3.492E-1	-2.891E-4	8.139E-8	-5.317E+5	

No	Formula	Name	Eq.	VP A	VP B	VP C	VP D	Tmin	Tmax	LDEN	TDEN
101	CHClF2	chlorodifluoromethane	1	-6.99913	1.23014	-2.49377	-2.21052	170	TC	1.23	289
102	CHCl2F	dichloromonofluoromethane	2	47.943	4629.02	-5.590	1665.	250	TC	1.38	282
103	CHCl3	chloroform	1	-6.95546	1.16625	-2.13970	-3.44421	215	TC	1.489	293
104	CHF3	fluoroform	1	-7.41994	1.65884	-3.14962	-0.84938	125	TC	1.246	239
105	CHN	hydrogen cyanide	2	31.122	4183.37	-3.004	1635.	280	TC	0.688	293
106	CH2Br2	dibromomethane	1	-7.35739	2.17546	-4.07038	3.50701	233	TC	2.50	293
107	CH2Cl2	dichloromethane	1	-7.44206	1.51914	-2.75319	-0.97949	155	TC	1.317	298
108	CH2F2	difluoromethane	1	-7.29343	1.08395	-1.63882	-2.30677	184	TC	0.815	253
109	CH2O	formaldehyde									
110	CH2O2	formic acid	3	10.3680	3599.58	-26.09		271	409	1.226	288
111	CH3Br	methyl bromide	1	-7.43951	3.15408	-4.67922	2.33796	184	TC	1.737	268
112	CH3Cl	methyl chloride	1	-6.86672	1.52273	-1.92919	-2.61459	175	TC	0.915	293
113	CH3F	methyl fluoride	1	-6.78099	0.828379	-1.41137	-2.41700	135	TC	0.843	213
114	CH3I	methyl iodide	1	-6.51125	0.888786	-1.36624	-3.03652	259	TC	2.279	293
115	CH3NO2	nitromethane	1	-8.41688	2.76466	-3.65341	-1.01376	328	TC	1.138	293
116	CH4	methane	1	-6.00435	1.18850	-0.83408	-1.22833	91	TC	0.425	112
117	CH4O	methanol	1	-8.54796	0.76982	-3.10850	1.54481	288	TC	0.791	293
118	CH4S	methyl mercaptan	1	-6.79300	1.52687	-2.45989	-1.34839	222	TC	0.866	293
119	CH5N	methyl amine	1	-7.52772	1.81615	-4.20677	-1.22275	200	TC	0.703	260
120	CH6N2	methyl hydrazine	3	8.5222	2319.84	-91.70		270	400		
121	CH6Si	methyl silane									
122	C2Br2ClF3	1,2-dibromo-1-chlorotrifluoroethane	1	-7.75667	2.65450	-4.26722	-0.10090	184	TC	2.175	294
123	C2Br2F4	1,2-dibromotetrafluoroethane	1	-7.30588	1.65554	-3.20770	-1.65654	225	TC	1.305	293
124	C2ClF3	chlorotrifluoroethene	1	-7.73622	2.58699	-4.21453	-0.15430	116	TC	1.26	303
125	C2ClF5	chloropentafluoroethane	1	-7.69084	2.41233	-4.48383	1.92058	174	TC		

No	Formula	Name	MolWt	Tfp K	Tb K	Tc K	Pc bar	Vc cm³/mol	Zc	Omega	Dipm debye
126	C2Cl2F4	1,1-dichlorotetrafluoroethane	170.922	179.	277.0	418.6	33.0	294.2	0.279	0.263	
127	C2Cl2F4	1,2-dichlorotetrafluoroethane	170.922	179.	276.2	418.9	32.6	293.8	0.275	0.246	0.5
128	C2Cl3F3	1,2,2-trichlorotrifluoroethane	187.380	238.2	320.8	487.3	34.1	325.5	0.274	0.256	
129	C2Cl4	tetrachloroethene	165.834	251.	394.4	620.2	47.6	289.6	0.250		0.0
130	C2Cl4F2	1,1,2,2-tetrachlorodifluoroethane	203.831	298.0	366.0	551.	38.7				0.0
131	C2F3N	trifluoroacetonitrile	95.023		205.5	311.1	36.2	202.	0.283	0.267	
132	C2F4	perfluoroethene	100.016	130.7	197.2	306.5	39.4	172.	0.267	0.223	
133	C2F6	perfluoroethane	138.012	172.4	194.9	293.0	30.6	222.	0.279		
134	C2N2	cyanogen	52.035	245.3	252.0	400.	59.8			0.278	0.0
135	C2HClF2	1-chloro-2,2-difluoroethene	98.479		254.6	400.6	44.6	197.	0.264	0.220	0.2
136	C2HClF4	chloro-1,1,2,2,-tetrafluoroethane	136.475		263.	399.9	37.2	244.	0.273	0.281	0.9
137	C2HCl3	trichloroethene	131.389	186.8	360.4	572.	50.5	256.	0.265	0.213	1.0
138	C2HCl5	pentachloroethane	202.295	244.	435.	646.	34.8				
139	C2HF3O2	trifluoroacetic acid	114.024	257.9	346.	491.3	32.6	204.	0.163	0.540	2.3
140	C2H2	acetylene	26.038		188.4	308.3	61.4	112.7	0.270	0.190	0.0
141	C2H2Cl2	cis-1,2-dichloroethene	96.944	192.7	333.3	537.	56.				1.8
142	C2H2Cl2	trans-1,2-dichloroethene	96.944	223.	321.9	513.	48.1			0.232	0.0
143	C2H2Cl4	1,1,2,2-tetrachloroethane	167.850	237.	419.4	661.2	58.4				1.5
144	C2H2F2	1,1-difluoroethene	64.035	129.	187.5	302.9	44.6	154.1	0.273	0.140	1.4
145	C2H2O	ketene	42.038	138.	232.	380.	65.	145.	0.30	0.21	1.4
146	C2H3Cl	vinyl chloride	62.499	119.4	259.8	425.	51.5	169.	0.265	0.122	1.5
147	C2H3ClF2	1-chloro-1,1-difluoroethane	100.496	142.	263.4	409.6	43.3	231.	0.294	0.251	2.1
148	C2H3ClO	acetyl chloride	78.498	160.2	323.9	508.0	58.7	204.	0.280	0.344	2.4
149	C2H3Cl3	1,1,1-trichloroethane	133.405	240.	347.2	545.	43.0				1.7
150	C2H3Cl3	1,1,2-trichloroethane	133.405	235.8	386.7	606.	51.4			0.217	1.4

No	Formula	Name	CPVAP A	CPVAP B	CPVAP C	CPVAP D	DELHF	DELGF
126	C2Cl2F4	1,1-dichlorotetrafluoroethane	4.045E+1	3.278E-1	-2.752E-4	7.821E-8		
127	C2Cl2F4	1,2-dichlorotetrafluoroethane	3.878E+1	3.440E-1	-2.950E-4	8.508E-8	-8.985E+5	
128	C2Cl3F3	1,2,2-trichlorotrifluoroethane	6.114E+1	2.874E-1	-2.420E-4	6.904E-8	-7.457E+5	
129	C2Cl4	tetrachloroethene	4.597E+1	2.255E-1	-2.294E-4	8.382E-8	-1.214E+4	2.261E+4
130	C2Cl4F2	1,1,2,2-tetrachlorodifluoroethane						
131	C2F3N	trifluoroacetonitrile	2.213E+1	2.519E-1	-2.361E-4	8.207E-8	-4.957E+5	-4.622E+5
132	C2F4	perfluoroethene	2.901E+1	2.277E-1	-2.036E-4	6.778E-8	-6.590E+5	-6.241E+5
133	C2F6	perfluoroethane	2.682E+1	3.458E-1	-2.869E-4	8.135E-8	-1.344E+6	-1.258E+6
134	C2N2	cyanogen	3.594E+1	9.253E-2	-8.148E-5	2.950E-8	3.092E+5	2.974E+5
135	C2HClF2	1-chloro-2,2-difluoroethene						
136	C2HClF4	chloro-1,1,2,2,-tetrafluoroethane						
137	C2HCl3	trichloroethene	3.017E+1	2.287E-1	-2.229E-4	8.244E-8	-5.862E+3	1.989E+4
138	C2HCl5	pentachloroethane	4.394E+1	3.374E-1	-3.356E-4	1.213E-7	-1.424E+5	-6.670E+4
139	C2HF3O2	trifluoroacetic acid						
140	C2H2	acetylene	2.682E+1	7.578E-2	-5.007E-5	1.412E-8	2.269E+5	2.093E+5
141	C2H2Cl2	cis-1,2-dichloroethene	1.161E+1	2.358E-1	-2.100E-4	7.242E-8	1.880E+3	2.437E+4
142	C2H2Cl2	trans-1,2-dichloroethene	1.828E+1	2.100E-1	-1.764E-4	5.804E-8	4.190E+3	2.660E+4
143	C2H2Cl4	1,2,2-tetrachloroethane	2.767E+1	3.251E-1	-2.974E-4	1.028E-7	-1.528E+5	-8.583E+4
144	C2H2F2	1,1-difluoroethene	3.073E+0	2.445E-1	-2.099E-4	7.021E-8	-3.454E+5	-3.217E+5
145	C2H2O	ketene	6.385E+0	1.638E-1	-1.084E-4	2.698E-8	-6.113E+4	-6.033E+4
146	C2H3Cl	vinyl chloride	5.949E+0	2.019E-1	-1.536E-4	4.773E-8	3.517E+4	5.154E+4
147	C2H3ClF2	1-chloro-1,1-difluoroethane	1.682E+1	2.757E-1	-1.992E-4	5.305E-8		
148	C2H3ClO	acetyl chloride	2.502E+1	1.711E-1	-9.856E-5	2.219E-8	-2.441E+5	-2.064E+5
149	C2H3Cl3	1,1,1-trichloroethane						
150	C2H3Cl3	1,1,2-trichloroethane	6.322E+0	3.431E-1	-2.958E-4	9.793E-8	-1.386E+5	-7.754E+4

No	Formula	Name	Eq.	VP A	VP B	VP C	VP D	Tmin	Tmax	LDEN	TDEN
126	C2Cl2F4	1,1-dichlorotetrafluoroethane	1	-7.33582	1.62482	-3.06234	-2.42281	217	TC	1.455	298
127	C2Cl2F4	1,2-dichlorotetrafluoroethane	1	-7.15825	1.10752	-2.12022	-4.54857	180	TC	1.48	277
128	C2Cl3F3	1,2,2-trichlorotrifluoroethane	1	-7.26519	1.39273	-2.50843	-5.26657	238	TC	1.580	289
129	C2Cl4	tetrachloroethene	1	-7.36067	1.82732	-3.47735	-1.00033	252	TC	1.62	293
130	C2Cl4F2	1,1,2,2-tetrachlorodifluoroethane	1	-7.80715	1.69009	-3.12042	-3.29269	299	TC	1.65	298
131	C2F3N	trifluoroacetonitrile	3	9.7917	1781.77	-23.28		142	206		
132	C2F4	perfluoroethene	1	-6.74371	0.62458	-1.94752	-3.78881	145	TC	1.519	197
133	C2F6	perfluoroethane	1	-7.32301	1.50248	-2.64678	-4.93429	173	TC	1.590	195
134	C2N2	cyanogen	2	51.703	4390.80	-6.185	1130.	250	TC	0.954	252
135	C2HClF2	1-chloro-2,2-difluoroethene	1	-7.19815	1.77543	-3.50534	-0.68772	136	TC		
136	C2HClF4	chloro-1,1,2,2,-tetrafluoroethane	1	-7.56490	1.81516	-3.54300	-1.04102	157	TC		
137	C2HCl3	trichloroethene	1	-7.38190	1.94817	-3.03294	-5.34536	291	TC	1.462	293
138	C2HCl5	pentachloroethane	1	-7.50052	1.16078	-3.48149	-1.04212	312	TC	1.671	298
139	C2HF3O2	trifluoroacetic acid	3	7.5356	2828.94	-57.11		285	345	1.535	273
140	C2H2	acetylene	1	-6.90128	1.26873	-2.09113	-2.75601	192	TC	0.615	189
141	C2H2Cl2	cis-1,2-dichloroethene	1	-6.97612	1.11972	-1.88483	-3.32030	274	TC	1.282	298
142	C2H2Cl2	trans-1,2-dichloroethene	1	-6.69776	1.08543	-2.90387	-0.25533	258	TC	1.255	293
143	C2H2Cl4	1,1,2,2-tetrachloroethane	1	-7.98542	2.49931	-4.07076	-0.69180	303	TC	1.600	293
144	C2H2F2	1,1-difluoroethene	1	-6.58895	0.90734	-0.82882	0.11779	130	TC	0.617	293
145	C2H2O	ketene	3	9.3995	1849.21	-35.15		170	255		297
146	C2H3Cl	vinyl chloride	1	-6.50008	1.21422	-2.57867	-2.00937	208	TC	0.969	259
147	C2H3ClF2	1-chloro-1,1-difluoroethane	1	-7.83556	2.79382	-4.42364	0.06334	143	TC	1.10	303
148	C2H3ClO	acetyl chloride	1	-7.94455	1.81437	-2.09194	-1.98959	267	TC	1.104	293
149	C2H3Cl3	1,1,1-trichloroethane	1	-7.31317	2.04642	-3.77747	-0.45475	247	TC	1.339	298
150	C2H3Cl3	1,1,2-trichloroethane	1	-7.71341	2.15518	-3.96435	-0.54604	323	TC	1.441	293

No	Formula	Name	MolWt	Tfp K	Tb K	Tc K	Pc bar	Vc cm³/mol	Zc	Omega	Dipm debye
151	C2H3F	vinyl fluoride	46.044	130.0	201.0	327.9	52.4	144.	0.277	0.157	1.4
152	C2H3F3	1,1,1-trifluoroethane	84.041	161.9	225.6	346.3	37.6	194.	0.253	0.251	2.3
153	C2H3N	acetonitrile	41.053	229.3	354.8	545.5	48.3	173.	0.184	0.327	3.5
154	C2H3NO	methyl isocyanate	57.052		312.	491.	55.7			0.278	
155	C2H4	ethylene	28.054	104.0	169.3	282.4	50.4	130.4	0.280	0.089	0.0
156	C2H4Br2	1,2-dibromoethane	187.862	283.3	404.7	646.	53.5	236.	0.275	0.795	1.0
157	C2H4Cl2	1,1-dichloroethane	98.960	176.2	330.5	523.	50.7	225.	0.259	0.240	2.0
158	C2H4Cl2	1,2-dichloroethane	98.960	237.5	356.7	566.	53.7	225.	0.253	0.278	1.8
159	C2H4F2	1,1-difluoroethane	66.051	156.2	248.2	386.7	45.0	181.	0.220	0.256	2.3
160	C2H4O	acetaldehyde	44.054	150.2	294.	461.	55.7	154.		0.303	2.5
161	C2H4O	ethylene oxide	44.054	161.	283.7	469.	71.9	140.	0.259	0.202	1.9
162	C2H4O2	acetic acid	60.052	289.8	391.1	592.7	57.9	171.	0.201	0.447	1.3
163	C2H4O2	methyl formate	60.052	174.2	304.9	487.2	60.0	172.	0.255	0.257	1.8
164	C2H5Br	ethyl bromide	108.966	154.6	311.5	503.9	62.3	215.	0.320	0.229	2.0
165	C2H5Cl	ethyl chloride	64.515	136.8	285.5	460.4	52.7	199.	0.274	0.191	2.0
166	C2H5F	ethyl fluoride	48.060	129.9	235.5	375.3	50.2	169.	0.272	0.215	2.0
167	C2H5I	ethyl iodide	155.967	165.	345.6	554.	47.0				1.7
168	C2H6	ethane	30.070	89.9	184.6	305.4	48.8	148.3	0.285	0.099	0.0
169	C2H6O	dimethyl ether	46.069	131.7	248.3	400.0	52.4	178.	0.287	0.200	1.3
170	C2H6O	ethanol	46.069	159.1	351.4	513.9	61.4	167.1	0.240	0.644	1.7
171	C2H6O2	ethylene glycol	62.069	260.2	470.5	(645.)	(77.)	207.	0.274	0.191	2.2
172	C2H6S	ethyl mercaptan	62.134	125.3	308.2	499.	54.9	201.	0.266	0.191	1.5
173	C2H6S	dimethyl sulfide	62.130	174.9	310.5	503.0	55.3	182.	0.270	0.289	1.5
174	C2H7N	ethyl amine	45.085	192.	289.7	456.4	56.4			0.289	1.3
175	C2H7N	dimethylamine	45.085	181.0	280.0	437.7	53.1			0.302	1.0

No	Formula	Name	CPVAP A	CPVAP B	CPVAP C	CPVAP D	DELHF	DELGF
151	C2H3F	vinyl fluoride					-1.172E+5	
152	C2H3F3	1,1,1-trifluoroethane	5.744E+0	3.141E-1	-2.597E-4	8.415E-8	-7.461E+5	-6.792E+5
153	C2H3N	acetonitrile	2.048E+1	1.196E-1	-4.492E-5	3.203E-9	8.792E+4	1.057E+5
154	C2H3N0	methyl isocyanate	3.576E+1	1.040E-1	-5.820E-6	-1.687E-8	-9.000E+4	
155	C2H4	ethylene	3.806E+0	1.566E-1	-8.348E-5	1.755E-8	5.234E+4	6.816E+4
156	C2H4Br2	1,2-dibromoethane	2.500E+1	2.517E-1	-1.833E-4	5.646E-8	-3.894E+4	-1.060E+4
157	C2H4Cl2	1,1-dichloroethane	1.247E+1	2.696E-1	-2.050E-4	6.301E-8	-1.300E+4	-7.314E+4
158	C2H4Cl2	1,2-dichloroethane	2.049E+1	2.310E-1	-1.438E-4	3.389E-8	-1.298E+5	-7.390E+4
159	C2H4F2	1,1-difluoroethane	8.675E+1	2.396E-1	-1.457E-4	3.394E-8	-4.940E+5	-4.365E+5
160	C2H4O	acetaldehyde	7.716E+0	1.823E-1	-1.007E-4	2.380E-8	-1.644E+5	-1.334E+5
161	C2H4O	ethylene oxide	-7.519E+0	2.222E-1	-1.256E-4	2.592E-8	-5.267E+4	-1.310E+4
162	C2H4O2	acetic acid	4.840E+0	2.549E-1	-1.753E-4	4.949E-8	-4.351E+5	-3.769E+5
163	C2H4O2	methyl formate	1.432E+0	2.700E-1	-1.949E-4	5.702E-8	-3.500E+5	-2.974E+5
164	C2H5Br	ethyl bromide	6.657E+0	2.348E-1	-1.472E-4	3.804E-8	-6.406E+4	-2.633E+4
165	C2H5Cl	ethyl chloride	-5.527E-1	2.606E-1	-1.840E-4	5.548E-8	-1.118E+5	-6.004E+4
166	C2H5F	ethyl fluoride	4.346E+0	2.180E-1	-1.166E-4	2.410E-8	-2.617E+5	-2.097E+5
167	C2H5I	ethyl iodide	1.011E+1	2.253E-1	-1.382E-4	3.531E-8	-8.370E+3	2.135E+4
168	C2H6	ethane	5.409E+0	1.781E-1	-6.938E-5	8.713E-9	-8.474E+4	-3.295E+4
169	C2H6O	dimethyl ether	1.702E+1	1.791E-1	-5.234E-5	-1.918E-9	-1.842E+5	-1.130E+5
170	C2H6O	ethanol	9.014E-1	2.141E-1	-8.390E-5	1.373E-9	-2.350E+5	-1.684E+5
171	C2H6O2	ethylene glycol	3.570E+1	2.483E-1	-1.497E-4	3.010E-8	-3.896E+5	-3.047E+5
172	C2H6S	ethyl mercaptan	1.492E+1	2.351E-1	-1.356E-4	3.162E-8	-4.614E+4	-4.670E+3
173	C2H6S	dimethyl sulfide	2.430E+1	1.875E-1	-6.875E-5	4.099E-9	-3.756E+4	6.950E+3
174	C2H7N	ethyl amine	3.693E+0	2.752E-1	-1.583E-4	3.808E-8	-4.605E+4	3.730E+4
175	C2H7N	dimethylamine	-1.717E-1	2.695E-1	-1.329E-4	2.339E-8	-1.880E+4	6.800E+4

No	Formula	Name	Eq.	VP A	VP B	VP C	VP D	Tmin	Tmax	LDEN	TDEN
151	C2H3F	vinyl fluoride	1	-6.80471	1.67182	-3.29094	-0.69493	114	TC	0.681	263
152	C2H3F3	1,1,1-trifluoroethane	1	-7.87141	2.78418	-4.55799	0.56876	163	TC	0.782	293
153	C2H3N	acetonitrile	2	40.774	5392.43	-4.357	2615.	300	TC	0.958	293
154	C2H3NO	methyl isocyanate	3	9.7056	2480.37	-56.31		230	340	0.958	293
155	C2H4	ethylene	1	-6.32055	1.16819	-1.55935	-1.83552	105	TC	0.577	163
156	C2H4Br2	1,2-dibromoethane	1	-7.45007	2.22849	-3.97795	-0.24734	290	TC	2.180	293
157	C2H4Cl2	1,1-dichloroethane	2	49.613	5422.68	-5.726	2380.	280	TC	1.168	298
158	C2H4Cl2	1,2-dichloroethane	1	-7.36864	1.76727	-3.34295	-1.43530	260	TC	1.250	289
159	C2H4F2	1,1-difluoroethane	1	-7.40625	1.76980	-3.44560	-1.09392	157	TC	1.012	247
160	C2H4O	acetaldehyde	1	-7.04687	0.12142	-2.66037E-2	-5.90300	273	TC	0.778	293
161	C2H4O	ethylene oxide	1	-6.56234	0.42696	-1.25638	-3.18133	238	TC	0.899	273
162	C2H4O2	acetic acid	1	-7.83183	5.51929E-4	0.24709	-8.50462	304	TC	1.049	293
163	C2H4O2	methyl formate	1	-6.99601	0.89328	-2.52294	-3.16636	220	TC	0.974	293
164	C2H5Br	ethyl bromide	1	-9.14807	5.49831	-6.68657	6.27287	301	TC	1.451	298
165	C2H5Cl	ethyl chloride	1	-7.23667	2.11017	-3.53882	0.34775	217	TC	0.896	293
166	C2H5F	ethyl fluoride	1	-6.82738	0.59267	-0.73934	-3.69185	266	TC		
167	C2H5I	ethyl iodide	1	-6.50172	1.05321	-3.16148	-0.64188	290	TC	1.950	293
168	C2H6	ethane	1	-6.34307	1.01630	-1.19116	-2.03539	133	TC	0.548	183
169	C2H6O	dimethyl ether	1	-7.12597	1.81710	-3.10058	-0.91638	194	TC	0.667	293
170	C2H6O	ethanol	1	-8.51838	0.34163	-5.73683	8.32581	293	TC	0.789	293
171	C2H6O2	ethylene glycol	3	13.6299	6022.18	-28.25		364	494	1.114	293
172	C2H6S	ethyl mercaptan	1	-6.96578	1.50970	-2.73740	-1.73828	273	TC	0.839	293
173	C2H6S	dimethyl sulfide	1	-6.94973	1.43646	-2.51444	-2.47611	222	TC	0.848	293
174	C2H7N	ethyl amine	1	-7.20059	1.20679	-3.71972	-4.33511	215	TC	0.683	293
175	C2H7N	dimethyl amine	1	-7.90295	2.81577	-6.31338	-0.22407	240	TC	0.656	293

No	Formula	Name	MolWt	Tfp K	Tb K	Tc K	Pc bar	Vc cm³/mol	Zc	Omega	Dipm debye
176	C2H7NO	monoethanolamine	61.084	283.5	443.5	614.	44.5	196.	0.17		2.6
177	C2H8N2	ethylenediamine	60.099	284.	390.4	593.	62.8	206.	0.26	0.51	1.9
178	C3ClF5O	chloropentafluoroacetone	182.475		281.0	410.6	28.8			0.347	
179	C3F6O	perfluoroacetone	166.020		245.7	357.1	28.4	329.	0.314	0.365	
180	C3F8	perfluoropropane	188.017	90.	236.5	345.1	26.8	299.8	0.280	0.325	
181	C3H3F3	trifluoropropene	96.051		244.	376.2	38.0	211.	0.256	0.238	
182	C3H3F5	1,1,1,2,2-pentafluoropropane	134.047		255.7	380.1	31.4	273.	0.271	0.308	
183	C3H3N	acrylonitrile	53.064	189.5	350.5	536.	45.6	210.	0.21	0.35	3.5
184	C3H3NO	isoxazole	69.063		368.	552.					2.8
185	C3H4	propadiene	40.065	136.9	238.7	393.	54.7	162.	0.271	0.313	0.2
186	C3H4	methyl acetylene	40.065	170.5	249.9	402.4	56.3	164.	0.275	0.215	0.7
187	C3H4O	acrolein	56.064	186.	326.	506.	51.6	210.	0.23	0.33	2.9
188	C3H4O2	acrylic acid	72.064	285.	414.	615.	56.7	210.	0.31	0.56	
189	C3H4O2	vinyl formate	72.064	215.5	319.6	475.	57.7			0.55	
190	C3H5Cl	allyl chloride	76.526	138.7	318.3	514.	47.6	234.	0.26	0.13	2.0
191	C3H5Cl3	1,2,3-trichloropropane	147.432	258.5	429.	651.	39.5	348.	0.25	0.31	1.6
192	C3H5N	propionitrile	55.080	180.3	370.3	564.4	41.8	229.	0.205	0.313	3.7
193	C3H6	cyclopropane	42.081	145.7	240.3	397.8	54.9	163.	0.274	0.130	0.0
194	C3H6	propylene	42.081	87.9	225.5	364.9	46.0	181.	0.274	0.144	0.4
195	C3H6Cl2	1,2-dichloropropane	112.987	172.7	369.5	577.	44.5	226.	0.21	0.24	1.9
196	C3H6O	acetone	58.080	178.2	329.2	508.1	47.0	209.	0.232	0.304	2.9
197	C3H6O	allyl alcohol	58.080	144.	370.2	543.0	63.3				
198	C3H6O	propionaldehyde	58.080	193.	321.	515.3	49.2	186.	0.229	0.313	2.7
199	C3H6O	1,2-propylene oxide	58.080	161.	308.	482.2	47.6	205.	0.27	0.269	2.0
200	C3H6O	vinyl methyl ether	58.080	151.5	278.	436.				0.34	

No	Formula	Name	CPVAP A	CPVAP B	CPVAP C	CPVAP D	DELHF	DELGF
176	C2H7NO	monoethanolamine	9.311E+0	3.009E-1	-1.818E-4	4.656E-8	-2.017E+5	
177	C2H8N2	ethylenediamine	3.830E+1	2.407E-1	-4.338E-5	-3.948E-8		
178	C3C1F5O	chloropentafluoroacetone						
179	C3F6O	perfluoroacetone						
180	C3F8	perfluoropropane						
181	C3H3F3	trifluoropropene						
182	C3H3F5	1,1,1,2,2-pentafluoropropane						
183	C3H3N	acrylonitrile	1.069E+1	2.208E-1	-1.565E-4	4.601E-8	1.851E+5	1.954E+5
184	C3H3NO	isoxazole						
185	C3H4	propadiene	9.906E+0	1.977E-1	-1.182E-4	2.782E-8	1.923E+5	2.025E+5
186	C3H4	methyl acetylene	1.471E+1	1.864E-1	-1.174E-4	3.224E-8	1.856E+5	1.946E+5
187	C3H4O	acrolein	1.197E+1	2.106E-1	-1.071E-4	1.906E-8	-7.092E+4	-6.519E+4
188	C3H4O2	acrylic acid	1.742E+0	3.191E-1	-2.352E-4	6.975E-8	-3.365E+5	-2.863E+5
189	C3H4O2	vinyl formate	2.781E+1	1.839E-1	-3.560E-5	-2.335E-7	-6.280E+2	4.363E+4
190	C3H5C1	allyl chloride	2.529E+0	3.047E-1	-2.278E-4	7.293E-8		
191	C3H5C13	1,2,3-trichloropropane	2.688E+1	3.622E-1	-2.787E-4	8.788E-8	-1.859E+5	-9.785E+4
192	C3H5N	propionitrile	1.540E+1	2.245E-1	-1.100E-4	1.954E-8	5.066E+4	9.621E+4
193	C3H6	cyclopropane	-3.524E+1	3.813E-1	-2.881E-4	9.035E-8	5.334E+4	1.045E+5
194	C3H6	propylene	3.710E+0	2.345E-1	-1.160E-4	2.205E-8	2.043E+4	6.276E+4
195	C3H6C12	1,2-dichloropropane	1.045E+1	3.655E-1	-2.604E-4	7.741E-8	-1.660E+5	-8.315E+4
196	C3H6O	acetone	6.301E+0	2.606E-1	-1.253E-4	2.038E-8	-2.177E+5	-1.532E+5
197	C3H6O	allyl alcohol	-1.105E+0	3.146E-1	-2.032E-4	5.321E-8	-1.321E+5	-7.130E+4
198	C3H6O	propionaldehyde	1.172E+1	2.614E-1	-1.300E-4	2.126E-8	-1.922E+5	-1.305E+5
199	C3H6O	1,2-propylene oxide	-8.457E+0	3.257E-1	-1.989E-4	4.823E-8	-9.282E+4	-1.305E+5
200	C3H6O	vinyl methyl ether	1.563E+1	2.341E-1	-9.697E-5	1.062E-8		-2.580E+4

No	Formula	Name	Eq.	VP A	VP B	VP C	VP D	Tmin	Tmax	LDEN	TDEN
176	C2H7NO	monoethanolamine	1	-10.8842	3.03743	-7.21939	-2.99322	379	TC	1.016	293
177	C2H8N2	ethylenediamine	1	-8.82254	2.27867	-3.52636	-6.97579	285	TC	0.896	293
178	C3ClF5O	chloropentafluoroacetone									
179	C3F6O	perfluoroacetone									
180	C3F8	perfluoropropane	3	9.3122	1901.54	-31.97		194	237	1.350	293
181	C3H3F3	trifluoropropene									
182	C3H3F5	1,1,2,2-pentafluoropropane									
183	C3H3N	acrylonitrile	3	9.3051	2782.21	-51.15		255	385	0.806	293
184	C3H3NO	isoxazole								1.078	293
185	C3H4	propadiene	3	6.5361	1054.72	-77.08		174	257	0.658	238
186	C3H4	methyl acetylene	1	-7.43860	2.62026	-5.76535	7.55261	178	TC	0.706	223
187	C3H4O	acrolein	3	9.2855	2606.53	-45.15		235	360	0.839	293
188	C3H4O2	acrylic acid	3	9.9415	3319.18	-80.15		315	450	1.051	293
189	C3H4O2	vinyl formate	3	10.0329	2569.68	-63.15		240	350	0.963	293
190	C3H5Cl	allyl chloride	1	-6.76334	2.50730	-7.64033	11.6666	286	TC	0.937	293
191	C3H5Cl3	1,2,3-trichloropropane	3	9.5044	3417.27	-69.15		315	470	1.389	293
192	C3H5N	propionitrile	1	-7.27719	0.46035	-0.45714	-10.1636	309	TC	0.782	293
193	C3H6	cyclopropane	1	-7.98411	4.38160	-5.72309	3.40444	183	TC	0.563	288
194	C3H6	propylene	1	-6.64231	1.21857	-1.81005	-2.48212	140	TC	0.612	223
195	C3H6Cl2	1,2-dichloropropane	1	-6.82259	0.54655	-1.59982	-5.05429	318	TC	1.15	293
196	C3H6O	acetone	1	-7.45514	1.20200	-2.43926	-3.35590	259	TC	0.790	293
197	C3H6O	allyl alcohol	3	10.2864	2928.20	-85.15		286	400	0.855	288
198	C3H6O	propionaldehyde	1	-7.18479	1.00298	-1.49247	-5.13288	235	TC	0.797	293
199	C3H6O	1,2-propylene oxide	1	-6.97569	0.63650	-1.49187	-6.37743	249	TC	0.829	293
200	C3H6O	vinyl methyl ether	3	7.8400	1980.22	-25.15		190	315	0.750	293

No	Formula	Name	MolWt	Tfp K	Tb K	Tc K	Pc bar	Vc cm³/mol	Zc	Omega	Dipm debye
201	C3H6O2	propionic acid	74.080	252.5	414.5	612.	54.	222.	0.183	0.520	1.5
202	C3H6O2	ethyl formate	74.080	193.8	327.5	508.5	47.4	229.	0.257	0.285	2.0
203	C3H6O2	methyl acetate	74.080	175.	330.4	506.8	46.9	228.	0.254	0.326	1.7
204	C3H7Cl	propyl chloride	78.542	150.4	320.4	503.	45.8	254.	0.278	0.235	2.0
205	C3H7Cl	isopropyl chloride	78.542	156.0	308.9	485.0	47.2	230.	0.269	0.232	2.1
206	C3H8	propane	44.094	85.5	231.1	369.8	42.5	203.	0.281	0.153	0.0
207	C3H8O	1-propanol	60.096	146.9	370.3	536.8	51.7	219.	0.253	0.623	1.7
208	C3H8O	isopropyl alcohol	60.096	184.7	355.4	508.3	47.6	220.	0.248	0.665	1.7
209	C3H8O	methyl ethyl ether	60.096	134.	280.6	437.8	44.0	221.	0.267	0.244	1.2
210	C3H8O2	methylal	76.096	168.	315.	480.6	39.5	213.	0.211	0.286	1.0
211	C3H8O2	1,2-propanediol	76.096	213.	460.5	625.	60.7	237.	0.28		3.6
212	C3H8O2	1,3-propanediol	76.096	246.4	487.6	724.	89.5				3.7
213	C3H8O3	glycerol	92.095	291.	563.	726.	66.8		0.28		3.0
214	C3H8S	methyl ethyl sulfide	76.157	167.2	339.8	533.	42.6	255.		0.216	
215	C3H9BO3	trimethyl borate	103.912		342.	501.7	35.9			0.415	0.8
216	C3H9N	n-propyl amine	59.112	190.	321.7	497.0	48.1	233.	0.271	0.303	1.3
217	C3H9N	isopropyl amine	59.112	177.9	305.6	471.8	45.4	221.	0.255	0.291	
218	C3H9N	trimethyl amine	59.112	156.	276.0	433.3	40.9	254.	0.288	0.205	0.6
219	C4F8	perfluorocyclobutane	200.028		267.2	388.5	27.8	324.	0.279	0.356	
220	C4F10	perfluorobutane	238.024	145.	271.2	386.4	23.2	378.	0.274	0.374	
221	C4H4	vinylacetylene	52.076	227.6	278.1	455.	49.6	202.	0.26	0.092	
222	C4H4O	furan	68.075	187.5	304.5	490.2	55.0	218.	0.295	0.209	0.7
223	C4H4S	thiophene	84.136	234.9	357.2	579.4	56.9	219.	0.258	0.196	0.5
224	C4H5N	allyl cyanide	67.091	186.7	392.	585.	39.5	265.	0.22	0.39	3.4
225	C4H5N	pyrrole	67.091		403.0	639.8					1.8

No	Formula	Name	CPVAP A	CPVAP B	CPVAP C	CPVAP D	DELHF	DELGF
201	C3H6O2	propionic acid	5.669E+0	3.689E-1	-2.865E-4	9.877E-8	-4.554E+5	-3.696E+5
202	C3H6O2	ethyl formate	2.467E+1	2.316E-1	-2.120E-5	-5.359E-8	-3.715E+5	
203	C3H6O2	methyl acetate	1.655E+1	2.245E-1	-4.342E-5	2.914E-8	-4.097E+5	
204	C3H7Cl	propyl chloride	-3.345E+0	3.626E-1	-2.508E-4	7.448E-8	-1.302E+5	-5.070E+4
205	C3H7Cl	isopropyl chloride	1.842E+0	3.488E-1	-2.244E-4	5.862E-8	-1.465E+5	-6.255E+4
206	C3H8	propane	-4.224E+0	3.063E-1	-1.586E-4	3.215E-8	-1.039E+5	-2.349E+4
207	C3H8O	1-propanol	2.470E+0	3.325E-1	-1.855E-4	4.296E-8	-2.566E+5	-1.619E+5
208	C3H8O	isopropyl alcohol	3.243E+1	1.885E-1	6.406E-5	-9.261E-8	-2.726E+5	-1.735E+5
209	C3H8O	methyl ethyl ether	1.867E+1	2.685E-1	-1.025E-4	8.951E-9	-2.166E+5	-1.177E+5
210	C3H8O2	methylal						
211	C3H8O2	1,2-propanediol	6.322E-1	4.212E-1	-2.981E-4	8.951E-8	-4.242E+5	
212	C3H8O2	1,3-propanediol	8.269E+0	3.676E-1	-2.162E-4	5.053E-8	-4.091E+5	
213	C3H8O3	glycerol	8.424E+0	4.442E-1	-3.159E-4	9.378E-8	-5.853E+5	
214	C3H8S	methyl ethyl sulfide	1.953E+1	2.891E-1	-1.209E-4	1.287E-8	-5.966E+4	1.140E+4
215	C3H9BO3	trimethyl borate						
216	C3H9N	n-propyl amine	6.691E+0	3.498E-1	-1.822E-4	3.586E-8	-7.243E+4	3.982E+4
217	C3H9N	isopropyl amine	-7.486E+0	4.175E-1	-2.826E-4	8.348E-8	-8.382E+4	
218	C3H9N	trimethyl amine	-8.206E+0	3.972E-1	-2.219E-4	4.622E-8	-2.386E+4	9.898E+4
219	C4F8	perfluorocyclobutane						
220	C4F10	perfluorobutane						
221	C4H4	vinylacetylene	6.757E+0	2.841E-1	-2.265E-4	7.461E-8	3.048E+5	3.062E+5
222	C4H4O	furan	-3.553E+1	4.321E-1	-3.455E-4	1.074E-7	-3.470E+4	8.790E+2
223	C4H4S	thiophene	-3.061E+1	4.480E-1	-3.772E-4	1.253E-7	1.158E+5	1.269E+5
224	C4H5N	allyl cyanide	2.170E+1	2.572E-1	-1.192E-4	1.229E-8		
225	C4H5N	pyrrole					1.084E+5	

No	Formula	Name	Eq.	VP A	VP B	VP C	VP D	Tmin	Tmax	LDEN	TDEN
201	C3H6O2	propionic acid	1	-8.69958	1.49460	-4.50355	1.06898	345	TC	0.993	293
202	C3H6O2	ethyl formate	1	-7.16968	1.13188	-3.37309	-3.53058	277	TC	0.927	289
203	C3H6O2	methyl acetate	1	-8.05406	2.56375	-5.12994	0.16125	275	TC	0.934	293
204	C3H7Cl	propyl chloride	1	-7.55764	2.60153	-5.06041	3.31163	248	TC	0.891	293
205	C3H7Cl	isopropyl chloride	3	9.4182	2490.48	-43.15		225	340	0.862	293
206	C3H8	propane	1	-6.72219	1.33236	-2.13868	-1.38551	145	TC	0.582	231
207	C3H8O	1-propanol	1	-8.05594	4.25183E-2	-7.51296	6.89004	260	TC	0.804	293
208	C3H8O	isopropyl alcohol	1	-8.16927	-9.43213E-2	-8.10040	7.85000	250	TC	0.786	293
209	C3H8O	methyl ethyl ether	1	-7.64466	2.88475	-6.32922	0.33736	224	TC	0.700	293
210	C3H8O2	methylal	3	9.2035	2415.92	-52.58		270	315	0.888	291
211	C3H8O2	1,2-propanediol	3	13.9122	6091.95	-22.46		357	483	1.036	293
212	C3H8O2	1,3-propanediol	1	-10.20156	2.93938	-6.69889	5.49989	332	TC	1.053	293
213	C3H8O3	glycerol	3	10.6190	4487.04	-140.2		440	600	1.261	293
214	C3H8S	methyl ethyl sulfide	3	9.3563	2722.95	-48.37		250	360	0.837	293
215	C3H9O3	trimethyl borate								0.915	293
216	C3H9N	n-propyl amine	1	-7.23587	1.22853	-3.75004	-4.33990	235	TC	0.717	293
217	C3H9N	isopropyl amine	1	-7.40866	1.79229	-4.75675	-1.70138	235	TC	0.688	293
218	C3H9N	trimethyl amine	1	-6.88066	1.15962	-2.18332	-2.94707	200	TC	0.633	293
219	C4F8	perfluorocyclobutane	3	9.0726	1985.95	-48.01		241	274	1.654	253
220	C4F10	perfluorobutane	3	9.5788	2280.18	-32.82		233	272	1.517	293
221	C4H4	vinylacetylene	3	9.3898	2203.57	-43.15		200	305	0.710	273
222	C4H4O	furan	3	9.4410	2442.70	-45.41		238	363	0.938	293
223	C4H4S	thiophene	1	-7.05208	1.69640	-3.17778	-1.57742	312	TC	1.071	289
224	C4H5N	allyl cyanide	3	9.3817	3128.75	-58.15		400	430	0.835	293
225	C4H5N	pyrrole	3	10.1764	3457.47	-62.73		330	440	0.967	294

No	Formula	Name	MolWt	Tfp K	Tb K	Tc K	Pc bar	Vc cm³/mol	Zc	Omega	Dipm debye
226	C4H6	1-butyne	54.092	147.4	281.2	463.7	47.1	220.	0.27	0.050	0.8
227	C4H6	2-butyne	54.092	240.9	300.1	488.7	50.8	221.	0.277	0.124	0.8
228	C4H6	1,2-butadiene	54.092	137.0	284.0	443.7	44.9	219.	0.267	0.255	0.4
229	C4H6	1,3-butadiene	54.092	164.2	268.7	425.	43.3	221.	0.270	0.195	0.0
230	C4H602	vinyl acetate	86.091	173.	346.	525.	43.5	265.	0.26	0.34	1.7
231	C4H603	acetic anhydride	102.089	199.	413.2	569.	46.8			0.908	3.0
232	C4H604	dimethyl oxalate	118.090	327.	436.5	628.	39.8			0.556	
233	C4H604	succinic acid	118.090	456.	508.						
234	C4H7N	butyronitrile	69.107	161.0	391.1	582.2	37.9			0.373	2.2
235	**C4H602**	methyl acrylate	86.091	196.7	353.5	536.	43.	265.	0.25	0.35	3.8
236	C4H8	1-butene	56.108	87.8	266.9	419.6	40.2	240.	0.277	0.191	0.3
237	C4H8	2-butene,cis	56.108	134.3	276.9	435.6	42.0	234.	0.271	0.202	0.3
238	C4H8	2-butene,trans	56.108	167.6	274.0	428.6	39.9	238.	0.266	0.205	0.0
239	C4H8	cyclobutane	56.108	182.4	285.7	460.0	49.9	210.	0.274	0.181	
240	C4H8	isobutylene	56.108	132.8	266.2	417.9	40.0	239.	0.275	0.194	0.5
241	C4H80	n-butyraldehyde	72.107	176.8	348.0	545.4	53.8	274.	0.27	0.352	2.6
242	C4H80	isobutyraldehyde	72.107	208.2	337.	513.	41.5	267.	0.252	0.35	
243	C4H80	methyl ethyl ketone	72.107	186.5	352.7	536.8	42.1	267.	0.252	0.320	3.3
244	C4H80	tetrahydrofuran	72.107	164.7	338.	540.1	51.9	224.	0.259	0.217	1.7
245	C4H80	vinyl ethyl ether	72.107	157.9	308.7	475.	40.7			0.268	1.3
246	C4H802	n-butyric acid	88.107	267.9	437.2	628.	52.7	290.	0.292	0.683	1.5
247	C4H802	isobutyric acid	88.107	227.2	427.9	609.	40.5	292.	0.234	0.623	1.3
248	C4H802	1,4-dioxane	88.107	285.	374.6	587.	52.1	238.	0.254	0.281	0.4
249	C4H802	ethyl acetate	88.107	189.6	350.3	523.2	38.3	286.	0.252	0.362	1.9
250	C4H802	methyl propionate	88.107	185.7	352.8	530.6	40.0	282.	0.256	0.350	1.7

No	Formula	Name	CPVAP A	CPVAP B	CPVAP C	CPVAP D	DELHF	DELGF
226	C4H6	1-butyne	1.255E+1	2.744E-1	-1.545E-4	3.450E-8	1.653E+5	2.022E+5
227	C4H6	2-butyne	1.593E+1	2.381E-1	-1.070E-4	1.753E-8	1.464E+5	1.856E+5
228	C4H6	1,2-butadiene	1.120E+1	2.724E-1	-1.468E-4	3.089E-8	1.623E+5	1.986E+5
229	C4H6	1,3-butadiene	-1.687E+0	3.419E-1	-2.340E-4	6.335E-8	1.102E+5	1.508E+5
230	C4H6O2	vinyl acetate	1.516E+1	2.795E-1	-8.805E-5	-1.660E-8	-3.160E+5	
231	C4H6O3	acetic anhydride	-2.313E+1	5.087E-1	-3.580E-4	9.835E-8	-5.761E+5	-4.770E+5
232	C4H6O4	dimethyl oxalate	1.507E+1	4.689E-1	-3.143E-4	7.938E-8		
233	C4H6O4	succinic acid						
234	C4H7N	butyronitrile	1.521E+1	3.206E-1	-1.638E-4	2.982E-8	3.410E+4	1.087E+5
235	**C4H6O2**	methyl acrylate	1.516E+1	2.796E-1	-8.805E-5	-1.660E-8		
236	C4H8	1-butene	-2.994E+0	3.532E-1	-1.990E-4	4.463E-8	-1.260E+2	7.134E+4
237	C4H8	2-butene,cis	4.396E-1	2.953E-1	-1.018E-4	-0.616E-9	-6.990E+3	6.590E+4
238	C4H8	2-butene,trans	1.832E+1	2.564E-1	-7.013E-5	-8.989E-9	-1.118E+4	6.301E+4
239	C4H8	cyclobutane	-5.025E+1	5.024E-1	-3.558E-4	1.047E-7	2.667E+4	1.101E+5
240	C4H8	isobutylene	1.605E+1	2.804E-1	-1.091E-4	9.098E-9	-1.691E+4	5.811E+4
241	C4H8O	n-butyraldehyde	1.408E+1	3.457E-1	-1.723E-4	2.887E-8	-2.052E+5	-1.148E+5
242	C4H8O	isobutyraldehyde	2.446E+1	3.356E-1	-2.057E-4	6.368E-8	-2.159E+5	-1.214E+5
243	C4H8O	methyl ethyl ketone	1.094E+1	3.559E-1	-1.900E-4	3.920E-8	-2.385E+5	-1.462E+5
244	C4H8O	tetrahydrofuran	1.910E+1	5.162E-1	-4.132E-4	1.454E-7	-1.843E+5	
245	C4H8O	vinyl ethyl ether	1.728E+1	3.236E-1	-1.471E-4	2.150E-8	-1.403E+5	
246	C4H8O2	n-butyric acid	1.174E+1	4.137E-1	-2.430E-4	5.531E-8	-4.762E+5	
247	C4H8O2	isobutyric acid	9.814E+0	4.668E-1	-3.720E-4	1.350E-7	-4.842E+5	
248	C4H8O2	1,4-dioxane	-5.357E+1	5.987E-1	-4.085E-4	1.062E-7	-3.153E+5	-1.809E+5
249	C4H8O2	ethyl acetate	7.235E+0	4.072E-1	-2.092E-4	2.855E-8	-4.432E+5	-3.276E+5
250	C4H8O2	methyl propionate	1.820E+1	3.140E-1	-9.353E-5	-1.828E-8		

No	Formula	Name	Eq.	VP A	VP R	VP C	VP D	Tmin	Tmax	LDEN	TDEN
226	C4H6	1-butyne	1	-6.29693	2.12358	-6.42124	4.11543	194	TC	0.650	289
227	C4H6	2-butyne	3	9.6669	2536.78	-37.34		240	320	0.691	293
228	C4H6	1,2-butadiene	3	9.4837	2397.26	-30.88		245	305	0.652	293
229	C4H6	1,3-butadiene	1	-7.12563	1.73913	-2.70805	-1.68376	197	TC	0.621	293
230	C4H6O2	vinyl acetate	1	-7.80478	1.80668	-4.48160	1.70357	295	TC	0.932	293
231	C4H6O3	acetic anhydride	1	-18.1529	18.3036	-20.0953	16.6970	336	TC	1.087	293
232	C4H6O4	dimethyl oxalate								1.15	288
233	C4H6O4	succinic acid									
234	C4H7N	butyronitrile	2	49.985	6476.68	-5.599	3770.	320	TC	0.792	293
235	**C4H6O2**	methyl acrylate	3	9.4886	2788.43	-59.15		260	390	0.956	293
236	C4H8	1-butene	1	-6.88204	1.27051	-2.26284	-2.61632	170	TC	0.595	293
237	C4H8	2-butene,cis	1	-6.88706	1.15941	-2.19304	-3.12758	203	TC	0.621	293
238	C4H8	2-butene,trans	2	43.517	4174.56	-5.041	1995.	240	400	0.604	293
239	C4H8	cyclobutane	1	-7.40011	2.37997	-3.12269	-0.34310	213	TC	0.694	293
240	C4H8	isobutylene	1	-6.95542	1.35673	-2.45222	-1.46110	170	TC	0.594	293
241	C4H8O	n-butyraldehyde	1	-7.01403	0.12265	-0.00073	-8.50911	304	TC	0.802	293
242	C4H8O	isobutyraldehyde	1	-7.53679	1.08548	-1.52929	-8.48589	286	TC	0.789	293
243	C4H8O	methyl ethyl ketone	1	-7.71476	1.71061	-3.68770	-0.75169	255	TC	0.805	293
244	C4H8O	tetrahydrofuran	3	9.4867	2768.38	-46.90		270	370	0.889	293
245	C4H8O	vinyl ethyl ether	1	-7.33727	1.50878	-3.30376	-1.10728	256	TC	0.793	293
246	C4H8O2	n-butyric acid	1	-10.0392	3.15679	-7.72604	5.27630	364	TC	0.958	293
247	C4H8O2	isobutyric acid	3	76.037	9222.72	-8.986	3863.	320	TC	0.968	293
248	C4H8O2	1,4-dioxane	3	9.5125	2966.88	-62.15		275	410	1.033	293
249	C4H8O2	ethyl acetate	1	-7.68521	1.36511	-4.08980	-1.75342	289	TC	0.901	293
250	C4H8O2	methyl propionate	1	-8.23756	2.71406	-5.35097	-2.34114	294	TC	0.915	293

No	Formula	Name	MolWt	Tfp K	Tb K	Tc K	Pc bar	Vc cm^3/mol	Zc	Omega	Dipm debye
251	C4H8O2	n-propyl formate	88.107	180.3	354.1	538.0	40.6	285.	0.259	0.314	1.9
252	C4H8S	tetrahydrothiophene	88.172	177.0	394.2	632.					1.9
253	C4H9Cl	1-chlorobutane	92.569	150.1	351.6	542.	36.8	312.	0.255	0.218	2.0
254	C4H9Cl	2-chlorobutane	92.569	141.8	341.4	520.6	39.5	305.	0.28	0.30	2.1
255	C4H9Cl	tert-butyl chloride	92.569	247.8	324.	507.	39.5	295.	0.28	0.19	2.1
256	C4H9N	pyrrolidine	71.123		359.6	568.6	56.1	249.	0.295	0.274	1.6
257	C4H9NO	morpholine	87.122	268.4	401.4	618.	54.7	253.	0.27	0.37	1.5
258	C4H10	n-butane	58.124	134.8	272.7	425.2	38.0	255.	0.274	0.199	0.0
259	C4H10	isobutane	58.124	113.6	261.4	408.2	36.5	263.	0.283	0.183	0.1
260	C4H10O	n-butanol	74.123	183.9	390.9	563.1	44.2	275.	0.259	0.593	1.8
261	C4H10O	2-butanol	74.123	158.5	372.7	536.1	41.8	269.	0.252	0.577	1.7
262	C4H10O	isobutanol	74.123	165.2	381.0	547.8	43.0	273.	0.257	0.592	1.7
263	C4H10O	tert-butanol	74.123	298.8	355.5	506.2	39.7	275.	0.259	0.612	1.7
264	C4H10O	diethyl ether	74.123	156.9	307.6	466.7	36.4	280.	0.262	0.281	1.3
265	C4H10O	methyl propyl ether	74.123		311.7	476.3	38.0			0.271	1.2
266	C4H10O	methyl isopropyl ether	74.123		303.9	464.5	37.6	271.	0.235	0.266	
267	C4H10O2	1,2-dimethoxyethane	90.123	202.	358.	536.	38.7			0.358	0.0
268	C4H10O3	diethylene glycol	106.122	265.	519.	681.	47.				
269	C4H10S	diethyl sulfide	90.184	169.2	365.3	557.	39.6	318.	0.272	0.292	1.6
270	C4H10S2	diethyl disulfide	122.244	171.7	427.1	642.					2.0
271	C4H11N	n-butyl amine	73.139	224.1	349.5	531.9	42.0			0.329	1.3
272	C4H11N	isobutyl amine	73.139	188.0	336.2	514.3	41.0	301.	0.271	0.368	1.2
273	C4H11N	diethyl amine	73.139	223.4	328.6	496.5	37.1			0.291	1.1
274	C5F12	perfluoropentane	288.031		302.4	420.6	20.5	473.	0.276	0.432	0.0
275	C5H2F6O2	hexafluoroacetylacetone	208.059		327.3	485.1	27.7			0.278	0.0

No	Formula	Name	CPVAP A	CPVAP B	CPVAP C	CPVAP D	DELHF	DELGF
251	C4H8O2	n-propyl formate						
252	C4H8S	tetrahydrothiophene						
253	C4H9Cl	1-chlorobutane	-2.613E+0	4.497E-1	-2.937E-4	8.081E-8	-1.474E+5	-3.881E+4
254	C4H9Cl	2-chlorobutane	-3.433E+0	4.559E-1	-2.981E-4	8.256E-8	-1.616E+5	-5.351E+4
255	C4H9Cl	tert-butyl chloride	-3.931E+0	4.652E-1	-2.886E-4	7.871E-8	-1.834E+5	-6.414E+4
256	C4H9N	pyrrolidine	-5.153E+1	5.338E-1	-3.240E-4	7.528E-8	-3.600E+3	1.148E+5
257	C4H9NO	morpholine	-4.280E+1	5.388E-1	-2.666E-4	4.199E-8		
258	C4H10	n-butane	9.487E+0	3.313E-1	-1.108E-4	-2.822E-9	-1.262E+5	-1.610E+4
259	C4H10	isobutane	-1.390E+0	3.847E-1	-1.846E-4	2.895E-8	-1.346E+5	-2.090E+4
260	C4H10O	n-butanol	3.266E+0	4.180E-1	-2.242E-4	4.685E-8	-2.749E+5	-1.509E+5
261	C4H10O	2-butanol	5.753E+0	4.245E-1	-2.328E-4	4.773E-8	-2.928E+5	-1.677E+5
262	C4H10O	isobutanol	-7.708E+0	4.689E-1	-2.884E-4	7.231E-8	-2.834E+5	-1.674E+5
263	C4H10O	tert-butanol	-4.861E+1	7.172E-1	-7.084E-4	2.920E-7	-3.128E+5	-1.778E+5
264	C4H10O	diethyl ether	2.142E+1	3.359E-1	-1.035E-4	-9.357E-9	-2.524E+5	-1.224E+5
265	C4H10O	methyl propyl ether	2.131E+1	3.390E-1	-1.127E-4	-2.855E-9	-2.379E+5	-1.100E+5
266	C4H10O	methyl isopropyl ether	1.353E+1	3.697E-1	-1.481E-4	1.205E-8	-2.522E+5	-1.210E+5
267	C4H10O2	1,2-dimethoxyethane	3.223E+1	3.567E-1	-1.336E-4	8.399E-9		
268	C4H10O3	diethylene glycol	7.306E+1	3.461E-1	-1.468E-4	1.846E-8	-5.715E+5	
269	C4H10S	diethyl sulfide	1.359E+1	3.959E-1	-1.780E-4	2.649E-8	-8.353E+4	1.780E+4
270	C4H10S2	diethyl disulfide	2.690E+1	4.601E-1	-2.710E-4	5.970E-8	-7.469E+4	2.227E+4
271	C4H11N	n-butyl amine	5.079E+0	4.476E-1	-2.407E-4	7.599E-8	-9.211E+4	4.924E+4
272	C4H11N	isobutyl amine	9.491E+0	4.430E-1	-2.110E-4	2.333E-8		
273	C4H11N	diethyl amine	2.039E+0	4.430E-1	-2.183E-4	3.653E-8	-7.243E+4	7.214E+4
274	C5F12	perfluoropentane						
275	C5H2F6O2	hexafluoroacetylacetone						

No	Formula	Name	Eq.	VP A	VP B	VP C	VP D	Tmin	Tmax	LDEN	TDEN
251	C4H8O2	n-propyl formate	1	-7.48563	1.71260	-5.16404	1.64290	299	TC	0.911	289
252	C4H8S	tetrahydrothiophene	3	9.3870	3160.1	-57.2		308	473	1.000	293
253	C4H9Cl	1-chlorobutane	1	-6.79852	0.78511	-2.31047	-5.83223	256	TC	0.886	293
254	C4H9Cl	2-chlorobutane	3	9.3705	2753.43	-47.15		250	375	0.873	293
255	C4H9Cl	tert-butyl chloride	3	9.1919	2567.15	-44.15		235	360	0.842	293
256	C4H9N	pyrrolidine	1	-7.73658	2.33495	-4.20213	-3.71251	316	TC	0.852	295
257	C4H9NO	morpholine	3	9.6162	3171.35	-71.15		300	440	1.000	293
258	C4H10	n-butane	1	-6.88709	1.15157	-1.99873	-3.13003	170	TC	0.579	293
259	C4H10	isobutane	1	-6.95579	1.50090	-2.52717	-1.49776	165	TC	0.557	293
260	C4H10O	n-butanol	1	-8.00756	0.53783	-9.34240	6.68692	275	TC	0.810	293
261	C4H10O	2-butanol	1	-7.80578	0.32456	-9.41265	2.64643	265	TC	0.807	293
262	C4H10O	isobutanol	3	10.2510	2874.73	-100.3		293	388	0.802	293
263	C4H10O	tert-butanol	3	10.2346	2658.29	-95.50		293	376	0.787	293
264	C4H10O -	diethyl ether	1	-7.29916	1.24828	-2.91931	-3.36740	250	TC	0.713	293
265	C4H10O	methyl propyl ether	1	-7.59830	2.01601	-3.70390	-1.64710	258	TC	0.738	293
266	C4H10O	methyl isopropyl ether	1	-7.06696	0.86497	-2.16269	-4.72211	252	TC	0.724	288
267	C4H10O2	1,2-dimethoxyethane	3	9.4039	2869.79	-53.15		262	393	0.867	293
268	C4H10O3	diethylene glycol	3	10.4124	4122.52	-122.5		402	560	1.116	293
269	C4H10S	diethyl sulfide	3	9.3329	2896.27	-54.49		260	390	0.837	293
270	C4H10S2	diethyl disulfide	3	9.4405	3421.57	-64.19		312	455	0.998	293
271	C4H11N	n-butyl amine	1	-7.91668	2.36401	-5.01170	-2.54215	255	TC	0.739	293
272	C4H11N	isobutyl amine	1	-8.41366	3.12108	-5.70064	-1.83920	248	TC	0.722	295
273	C4H11N	diethyl amine	1	-7.26796	1.15810	-3.91125	-1.17981	240	TC	0.707	293
274	C5F12	perfluoropentane						282	338		
275	C5H2F6O2	hexafluoroacetylacetone	3	9.5390	2470.33	-43.20					

No	Formula	Name	MolWt	Tfp K	Tb K	Tc K	Pc bar	Vc cm³/mol	Zc	Omega	Dipm debye
276	C5H4O2	furfural	96.085	234.5	434.9	670.	58.9			0.383	3.6
277	C5H5N	pyridine	79.102	231.5	388.4	620.0	56.3	254.	0.277	0.243	2.3
278	C5H6N2	2-methyl pyrazine	94.117		410.	634.3	50.1	283.	0.268	0.315	0.7
279	C5H6O	2-methyl furan	82.102		338.	527.	47.2	247.	0.266	0.270	0.9
280	C5H8	cyclopentene	68.119	138.1	317.4	506.0					
281	C5H8	1,2-pentadiene	68.119	135.9	318.0	503.	40.7	276.	0.269	0.173	
282	C5H8	1,3-pentadiene,trans	68.119	185.7	315.1	496.	39.9	275.	0.266	0.175	0.7
283	C5H8	1,4-pentadiene	68.119	124.9	299.1	478.	37.9	276.	0.263	0.104	0.4
284	C5H8	1-pentyne	68.119	167.5	313.3	493.5	40.5	278.	0.275	0.164	0.9
285	C5H8	2-methyl-1,3-butadiene	68.119	127.2	307.2	484.	38.5	276.	0.264	0.164	0.3
286	C5H8	3-methyl-1,2-butadiene	68.119	159.5	314.0	496.	41.1	267.	0.266	0.160	
287	C5H8O	cyclopentanone	84.118	222.5	403.9	634.6	51.1	268.	0.260	0.35	3.0
288	C5H8O	dihydropyran	84.118		359.	561.7	45.6	268.	0.262	0.247	1.4
289	C5H8O2	ethyl acrylate	100.118	201.	373.	552.	37.4	320.	0.261	0.400	
290	C5H10	cyclopentane	70.135	179.3	322.4	511.7	45.1	260.	0.275	0.196	0.0
291	C5H10	1-pentene	70.135	107.9	303.1	464.8	35.3	300.	0.31	0.233	0.4
292	C5H10	2-pentene,cis	70.135	121.7	310.1	476.	36.5			0.251	
293	C5H10	2-pentene,trans	70.135	132.9	309.5	475.	36.6			0.259	
294	C5H10	2-methyl-1-butene	70.135	135.6	304.3	465.	34.5			0.236	0.5
295	C5H10	2-methyl-2-butene	70.135	139.3	311.7	470.	34.5			0.244	
296	C5H10	3-methyl-1-butene	70.135	104.7	293.3	450.	35.1	333.	0.26	0.209	
297	C5H10O	valeraldehyde	86.134	182.	376.	554.	35.4			0.40	2.6
298	C5H10O	methyl n-propyl ketone	86.134	196.	375.4	561.1	36.9	301.	0.238	0.346	2.5
299	C5H10O	methyl isopropyl ketone	86.134	181.	367.5	553.4	38.5	310.	0.259	0.331	2.8
300	C5H10O	diethyl ketone	86.134	234.2	375.1	561.0	37.3	336.	0.269	0.344	2.7

No	Formula	Name	CPVAP A	CPVAP B	CPVAP C	CPVAP D	DELHF	DELGF
276	C5H4O2	furfural						
277	C5H5N	pyridine	3.979E+1	4.928E-1	-3.558E-4	1.004E-7	1.403E+5	1.903E+5
278	C5H6N2	2-methyl pyrazine						
279	C5H6O	2-methyl furan						
280	C5H8	cyclopentene	-4.151E+1	4.631E-1	-2.579E-4	5.434E-8	3.295E+4	1.109E+5
281	C5H8	1,2-pentadiene	8.826E+0	3.880E-1	-2.280E-4	5.246E-8	1.457E+5	2.106E+5
282	C5H8	1,3-pentadiene,trans	3.069E+1	2.811E-1	-6.711E-5	-2.352E-8	7.787E+4	1.468E+5
283	C5H8	1,4-pentadiene	6.996E+0	3.952E-1	-2.374E-4	5.598E-8	1.055E+5	1.704E+5
284	C5H8	1-pentyne	1.807E+1	3.511E-1	-1.913E-4	4.098E-8	1.444E+5	2.104E+5
285	C5H8	2-methyl-1,3-butadiene	-3.412E+0	4.585E-1	-3.337E-4	1.000E-7	7.578E+4	1.460E+5
286	C5H8	3-methyl-1,2-butadiene	1.469E+1	3.598E-1	-1.976E-4	4.262E-8	1.298E+5	1.987E+5
287	C5H8O	cyclopentanone	-4.064E+1	5.255E-1	-3.124E-4	7.130E-8	-1.928E+5	
288	C5H8O	dihydropyran						
289	C5H8O2	ethyl acrylate	1.681E+1	3.690E-1	-1.382E-4	-5.732E-9	-7.729E+4	3.860E+4
290	C5H10	cyclopentane	-5.362E+1	5.426E-1	-3.031E-4	6.485E-8		
291	C5H10	1-pentene	-1.340E-1	4.329E-1	-2.317E-4	4.681E-8	-2.093E+4	7.917E+4
292	C5H10	2-pentene,cis	-1.429E+1	4.601E-1	-2.541E-4	5.455E-8	-2.809E+4	7.189E+4
293	C5H10	2-pentene,trans	1.947E+0	4.182E-1	-2.178E-4	4.405E-8	-3.178E+4	6.996E+4
294	C5H10	2-methyl-1-butene	1.057E+1	3.997E-1	-1.946E-4	3.314E-8	-3.634E+4	6.565E+4
295	C5H10	2-methyl-2-butene	1.180E+1	3.509E-1	-1.117E-4	-5.807E-9	-4.258E+4	5.970E+4
296	C5H10	3-methyl-1-butene	2.174E+1	3.890E-1	-2.007E-4	4.011E-8	-2.897E+4	7.482E+4
297	C5H10O	valeraldehyde	1.424E+1	4.329E-1	-2.107E-4	3.162E-8	-2.280E+5	-1.084E+5
298	C5H10O	methyl n-propyl ketone	1.147E+0	4.802E-1	-2.818E-4	6.661E-8	-2.588E+5	-1.372E+5
299	C5H10O	methyl isopropyl ketone	-2.914E+0	4.991E-1	-2.935E-4	6.665E-8		
300	C5H10O	diethyl ketone	3.001E+1	3.939E-1	-1.907E-4	3.398E-8	-2.588E+5	-1.354E+5

No	Formula	Name	Eq.	VP A	VP B	VP C	VP D	Tmin	Tmax	LDEN	TDEN
276	C5H4O2	furfural	3	8.5214	2760.09	-110.4		328	434	1.159	293
277	C5H5N	pyridine	1	-7.07689	1.21511	-2.76681	-2.87472	340	TC	0.983	293
278	C5H6N2	2-methyl pyrazine								1.044	273
279	C5H6O	2-methyl furan								0.913	293
280	C5H8	cyclopentene	3	9.3154	2583.07	-39.70		244	378	0.772	293
281	C5H8	1,2-pentadiene	3	9.3095	2544.34	-44.30		250	340	0.693	293
282	C5H8	1,3-pentadiene,trans	3	9.2980	2541.69	-41.43		250	340	0.676	293
283	C5H8	1,4-pentadiene	3	9.1190	2344.02	-41.69		240	320	0.661	293
284	C5H8	1-pentyne	3	9.4227	2515.62	-45.97		230	335	0.690	293
285	C5H8	2-methyl-1,3-butadiene	1	-6.59262	1.28930	-3.89168	1.70215	257	TC	0.681	293
286	C5H8	3-methyl-1,2-butadiene	1	-6.71441	1.53531	-4.64262	2.99854	274	TC	0.686	293
287	C5H8O	cyclopentanone	1	-7.19551	1.16379	-2.52546	-3.28861	273	TC	0.950	293
288	C5H8O	dihydropyran									
289	C5H8O2	ethyl acrylate	3	9.4688	2974.94	-58.15		274	409	0.921	293
290	C5H10	cyclopentane	1	-6.51809	0.38442	-1.11706	-4.50275	289	TC	0.745	293
291	C5H10	1-pentene	1	-7.04875	1.17813	-2.45105	-2.21727	190	TC	0.640	293
292	C5H10	2-pentene,cis	1	-6.80160	0.54458	-1.55279	-5.68029	275	TC	0.656	293
293	C5H10	2-pentene,trans	1	-6.99461	1.00724	-2.42146	-2.51692	274	TC	0.649	293
294	C5H10	2-methyl-1-butene	1	-6.82990	0.72660	-2.15363	-3.62225	274	TC	0.650	293
295	C5H10	2-methyl-2-butene	1	-7.71438	1.95946	-3.15710	-2.22515	276	TC	0.662	293
296	C5H10	3-methyl-1-butene	1	-7.18870	1.42502	-2.27292	-2.04323	273	TC	0.627	293
297	C5H10O	valeraldehyde	3	9.5421	3030.20	-58.15		277	412	0.810	293
298	C5H10O	methyl n-propyl ketone	3	9.3829	2934.87	-62.25		275	410	0.806	293
299	C5H10O	methyl isopropyl ketone	3	7.5577	1993.12	-103.2		271	406	0.803	293
300	C5H10O	diethyl ketone	1	-7.70542	1.44422	-3.60173	-2.88141	330	TC	0.814	293

No	Formula	Name	MolWt	Tfp K	Tb K	Tc K	Pc bar	Vc cm³/mol	Zc	Omega	Dipm debye
301	C5H10O	2-methyl tetrahydrofuran	86.134		351.	537.	37.6	267.	0.225	0.264	
302	C5H10O	tetrahydropyran	86.134		361.	572.2	47.7	263.	0.263	0.218	1.6
303	C5H10O2	n-valeric acid	102.134	239.0	459.5	651.					
304	C5H10O2	isovaleric acid	102.134		449.7	634.					1.0
305	C5H10O2	isobutyl formate	102.134	178.	371.4	554.	37.3	352.	0.285	0.396	1.9
306	C5H10O2	n-propyl acetate	102.134	178.0	374.7	549.4	33.3	345.	0.252	0.391	1.8
307	C5H10O2	ethyl propionate	102.134	199.3	372.2	546.0	33.6	345.	0.256	0.391	1.8
308	C5H10O2	methyl butyrate	102.134	188.4	375.9	554.4	34.8	340.	0.257	0.380	1.7
309	C5H10O2	methyl isobutyrate	102.134	185.4	365.5	540.8	34.3	339.	0.259	0.362	2.0
310	C5H11N	piperidine	85.150	262.7	379.6	594.0	47.6	289.	0.280	0.251	1.2
311	C5H12	n-pentane	72.151	143.4	309.2	469.7	33.7	304.	0.263	0.251	0.0
312	C5H12	2-methyl butane	72.151	113.3	301.0	460.4	33.9	306.	0.271	0.227	0.1
313	C5H12	2,2-dimethylpropane	72.151	256.6	282.6	433.8	32.0	303.	0.269	0.197	0.0
314	C5H12O	1-pentanol	88.150	195.0	411.1	588.2	39.1	326.	0.26	0.579	1.7
315	C5H12O	2-methyl-1-butanol	88.150	203.	401.9	571.0	33.4				
316	C5H12O	3-methyl-1-butanol	88.150	156.	405.2	579.4					1.8
317	C5H12O	2-methyl-2-butanol	88.150	264.4	375.5	545.0	39.5				1.9
318	C5H12O	2,2-dimethyl-1-propanol	88.150	327.	386.3	549.0					
319	C5H12O	ethyl propyl ether	88.150	146.4	336.4	500.2	33.7	339.	0.275	0.333	1.2
320	C5H12O	butyl methyl ether	88.150	157.7	343.3	512.8	33.7	329.	0.260	0.316	1.3
321	C5H12O	tert-butyl methyl ether	88.150		328.3	496.4	33.7			0.269	1.2
322	C6BrF5	bromopentafluorobenzene	246.960		410.0	601.	30.4			0.355	
323	C6ClF5	chloropentafluorobenzene	202.509		391.1	570.8	32.4	376.	0.256	0.400	
324	C6Cl2F4	dichlorotetrafluorobenzene	218.964		430.9	626.	53.2			0.622	
325	C6Cl3F3	1,3,5-trichlorotrifluorobenzene	235.419		471.5	684.9	32.7	448.	0.257	0.426	

No	Formula	Name	CPVAP A	CPVAP B	CPVAP C	CPVAP D	DELHF	DELGF
301	C5H10O	2-methyl tetrahydrofuran						
302	C5H10O	tetrahydropyran						
303	C5H10O2	n-valeric acid	1.339E+1	5.033E-1	-2.931E-4	6.619E-8	-4.907E+5	-3.574E+5
304	C5H10O2	isovaleric acid						
305	C5H10O2	isobutyl formate	1.985E+1	4.034E-1	-1.436E-4	-7.402E-9		
306	C5H10O2	n-propyl acetate	1.542E+1	4.501E-1	-1.686E-4	-1.439E-8	-4.660E+5	
307	C5H10O2	ethyl propionate	1.985E+1	4.034E-1	-1.437E-4	-7.394E-9	-4.702E+5	-3.237E+5
308	C5H10O2	methyl butyrate						
309	C5H10O2	methyl isobutyrate						
310	C5H11N	piperidine	-5.307E+1	6.289E-1	-3.358E-4	6.427E-8	-4.903E+4	
311	C5H12	n-pentane	-3.626E+0	4.873E-1	-2.580E-4	5.305E-8	-1.465E+5	-8.370E+3
312	C5H12	2-methyl butane	-9.525E+0	5.066E-1	-2.729E-4	5.723E-8	-1.546E+5	-1.482E+4
313	C5H12	2,2-dimethylpropane	-1.659E+1	5.552E-1	-3.306E-4	7.633E-8	-1.661E+5	-1.524E+4
314	C5H12O	1-pentanol	3.869E+0	5.045E-1	-2.639E-4	5.120E-8	-2.989E+5	-1.461E+5
315	C5H12O	2-methyl-1-butanol	-9.483E+0	5.677E-1	-3.481E-4	8.637E-8	-3.027E+5	-1.657E+5
316	C5H12O	3-methyl-1-butanol	-9.542E+0	5.681E-1	-3.485E-4	8.650E-8	-3.023E+5	-1.654E+5
317	C5H12O	2-methyl-2-butanol	-1.209E+1	6.096E-1	-4.204E-4	1.228E-7	-3.299E+5	-1.255E+5
318	C5H12O	2,2-dimethyl-1-propanol	1.215E+1	5.397E-1	-3.160E-4	7.122E-8	-2.931E+5	
319	C5H12O	ethyl propyl ether						
320	C5H12O	butyl methyl ether						
321	C5H12O	tert-butyl methyl ether	2.534E+0	5.136E-1	-2.596E-4	4.303E-8	-2.931E+5	-1.255E+5
322	C6RrF5	bromopentafluorobenzene						
323	C6ClF5	chloropentafluorobenzene						
324	C6Cl2F4	dichlorotetrafluorobenzene						
325	C6Cl3F3	1,3,5-trichlorotrifluorobenzene						

No	Formula	Name	Eq.	VP A	VP B	VP C	VP D	Tmin	Tmax	LDEN	TDEN
301	C5H10O	2-methyl tetrahydrofuran								0.855	293
302	C5H10O	tetrahydropyran								0.886	288
303	C5H10O2	n-valeric acid	3	11.0104	4092.15	-86.55		350	495	0.939	293
304	C5H10O2	isovaleric acid	3	2.4671	588.09	-261.9		359	378	0.925	293
305	C5H10O2	isobutyl formate	1	-8.01454	2.05091	-4.38201	-2.85582	270	TC	0.885	293
306	C5H10O2	n-propyl acetate	1	-7.85524	1.43936	-4.30187	-3.04832	312	TC	0.887	293
307	C5H10O2	ethyl propionate	1	-8.55094	3.10067	-6.99241	3.45112	307	TC	0.895	289
308	C5H10O2	methyl butyrate	1	-7.77600	1.32028	-3.93963	-3.53112	275	TC	0.898	293
309	C5H10O2	methyl isobutyrate	1	-7.65814	1.29248	-3.85632	-3.49858	270	TC	0.891	293
310	C5H11N	piperidine	1	-7.56707	2.15002	-3.89030	-3.70363	316	TC	0.862	293
311	C5H12	n-pentane	1	-7.28936	1.53679	-3.08367	-1.02456	195	TC	0.626	293
312	C5H12	2-methyl butane	1	-7.12727	1.38996	-2.54302	-2.45657	220	TC	0.620	293
313	C5H12	2,2-dimethylpropane	1	-6.89153	1.25019	-2.28233	-4.74891	260	TC	0.591	293
314	C5H12O	1-pentanol	1	-8.97725	2.99791	-12.9596	8.84205	290	TC	0.815	293
315	C5H12O	2-methyl-1-butanol	1	-9.26305	3.86947	-15.3562	12.1464	308	TC	0.819	293
316	C5H12O	3-methyl-1-butanol	3	10.0925	3026.43	-104.1		298	426	0.810	293
317	C5H12O	2-methyl-2-butanol	1	-8.66602	3.46689	-14.1750	10.9679	298	TC	0.809	293
318	C5H12O	2,2-dimethyl-1-propanol	3	11.5134	3694.96	-65.00		328	406	0.783	327
319	C5H12O	ethyl propyl ether	1	-8.05820	2.35916	-4.51822	0.92352	275	TC	0.733	293
320	C5H12O	butyl methyl ether	1	-7.75110	1.87213	-3.80629	-1.81410	285	TC	0.744	293
321	C5H10O	tert-butyl methyl ether	1	-7.82516	2.95493	-6.94079	12.17416	287	TC		
322	C6BrF5	bromopentafluorobenzene									
323	C6ClF5	chloropentafluorobenzene	1	-8.02172	1.54665	-3.78361	-2.99849	309	TC		
324	C6Cl2F4	dichlorotetrafluorobenzene									
325	C6Cl3F3	1,3,5-trichlorotrifluorobenzene	1	-8.20940	1.68886	-4.17824	-1.54115	364	TC		

No	Formula	Name	MolWt	Tfp K	Tb K	Tc K	Pc bar	Vc cm³/mol	Zc	Omega	Dipm debye
326	C6F6	perfluorobenzene	186.056		353.4	516.7	33.0	335.	0.255	0.396	
327	C6F12	perfluorocyclohexane	300.047		326.0	457.2	24.3	459.	0.270	0.432	
328	C6F14	perfluoro-n-hexane	338.044	186.0	329.8	448.8	18.7	606.	0.303	0.514	0.0
329	C6F14	perfluoro-2-methylpentane	338.044		330.8	453.	18.2	550.	0.266	0.464	
330	C6F14	perfluoro-3-methylpentane	338.044		331.5	450.	16.9			0.476	
331	C6F14	perfluoro-2,3-dimethylbutane	338.044		332.9	463.	18.7	525.	0.256	0.394	
332	C6HF5	pentafluorobenzene	168.064		358.9	531.0	35.3	324.	0.260	0.373	
333	C6HF5O	pentafluorophenol	184.063		418.8	609.	40.0	348.	0.275	0.502	
334	C6H2F4	1,2,3,4-tetrafluorobenzene	150.074		367.5	550.8	37.9	313.	0.259	0.344	
335	C6H2F4	1,2,3,5-tetrafluorobenzene	150.074		357.6	535.3	37.5			0.346	
336	C6H2F4	1,2,4,5-tetrafluorobenzene	150.074		363.4	543.4	38.0			0.355	
337	C6H4Cl2	o-dichlorobenzene	147.004	256.1	452.0	729.	41.0	360.	0.244	0.272	2.3
338	C6H4F2	1,4-difluorobenzene	114.094		362.0	556.	44.0			0.299	
339	C6H5Br	bromobenzene	157.010	242.3	429.2	670.0	45.2	324.	0.263	0.251	1.5
340	C6H5Cl	chlorobenzene	112.559	227.6	404.9	632.4	45.2	308.	0.265	0.249	1.6
341	C6H5F	fluorobenzene	96.104	234.0	357.9	560.1	45.5	269.	0.263	0.244	1.4
342	C6H5I	iodobenzene	204.011	241.8	461.6	721.0	45.2	351.	0.265	0.249	1.4
343	C6H6	benzene	78.114	278.7	353.2	562.2	48.9	259.	0.271	0.212	0.0
344	C6H6O	phenol	94.113	314.0	455.0	694.2	61.3	229.	0.240	0.438	1.6
345	C6H7N	aniline	93.129	267.0	457.6	699.	53.1	274.	0.250	0.384	1.6
346	C6H7N	2-methylpyridine	93.129	207.	402.6	621.	46.0	311.	0.260	0.299	1.9
347	C6H7N	3-methylpyridine	93.129		417.3	645.					2.4
348	C6H7N	4-methylpyridine	93.129	276.9	418.5	646.0	44.6			0.301	
349	C6H10	1,5-hexadiene	82.146	132.0	332.6	507.0	34.4			0.160	
350	C6H10	cyclohexene	82.146	169.7	356.1	560.5	43.4			0.210	0.6

No	Formula	Name	CPVAP A	CPVAP B	CPVAP C	CPVAP D	DELHF	DELGF
326	C6F6	perfluorobenzene	3.628E+1	5.267E-1	-4.547E-4	1.456E-7	-9.573E+5	-8.800E+5
327	C6F12	perfluorocyclohexane						
328	C6F14	perfluoro-n-hexane						
329	C6F14	perfluoro-2-methylpentane						
330	C6F14	perfluoro-3-methylpentane						
331	C6F14	perfluoro-2,3-dimethylbutane						
332	C6HF5	pentafluorobenzene						
333	C6HF50	pentafluorophenol						
334	C6H2F4	1,2,3,4-tetrafluorobenzene						
335	C6H2F4	1,2,3,5-tetrafluorobenzene						
336	C6H2F4	1,2,4,5-tetrafluorobenzene						
337	C6H4Cl2	o-dichlorobenzene	-1.430E+1	5.506E-1	-4.513E-4	1.429E-7	3.000E+4	8.273E+4
338	C6H4F2	1,4-difluorobenzene	-2.596E+1	5.722E-1	-4.677E-4	1.475E-7	-3.074E+5	-2.530E+5
339	C6H5Br	bromobenzene	-2.881E+1	5.351E-1	-4.080E-4	1.212E-7	1.051E+5	1.386E+5
340	C6H5Cl	chlorobenzene	-3.389E+1	5.631E-1	-4.522E-4	1.426E-7	5.187E+4	9.923E+4
341	C6H5F	fluorobenzene	-3.873E+1	5.669E-1	-4.434E-4	1.355E-7	-1.166E+5	-6.908E+4
342	C6H5I	iodobenzene	-2.927E+1	5.564E-1	-4.509E-4	1.443E-7	1.627E+5	1.879E+5
343	C6H6	benzene	-3.392E+1	4.739E-1	-3.017E-4	7.130E-8	8.298E+4	1.297E+5
344	C6H6O	phenol	-3.584E+1	5.983E-1	-4.827E-4	1.527E-7	-9.642E+4	-3.290E+4
345	C6H7N	aniline	-4.052E+1	6.385E-1	-5.133E-4	1.633E-7	8.692E+4	1.668E+5
346	C6H7N	2-methylpyridine	-3.626E+1	5.584E-1	-3.704E-4	9.663E-8	9.902E+4	1.772E+5
347	C6H7N	3-methylpyridine	-3.709E+1	5.600E-1	-3.719E-4	9.685E-8	1.062E+5	1.844E+5
348	C6H7N	4-methylpyridine	-1.743E+1	4.882E-1	-2.798E-4	5.451E-8	1.023E+5	
349	C6H10	1,5-hexadiene					8.374E+4	
350	C6H10	cyclohexene	-6.865E+1	7.252E-1	-5.414E-4	1.644E-7	-5.360E+3	1.069E+5

No	Formula	Name	Eq.	VP A	VP B	VP C	VP D	Tmin	Tmax	LDEN	TDEN
326	C6F6	perfluorobenzene	1	-7.97271	1.43798	-3.62195	-4.79241	278	TC		
327	C6F12	perfluorocyclohexane	3	7.2885	1374.07	-136.8		280	400		
328	C6F14	perfluoro-n-hexane	1	-9.16184	2.97539	-7.17322	5.50684	270	TC		
329	C6F14	perfluoro-2-methylpentane	3	9.6896	2760.0	-45.70		259	346	1.733	293
330	C6F14	perfluoro-3-methylpentane	3	9.2670	2565.44	-54.23		255	333		
331	C6F14	perfluoro-2,3-dimethylbutane	3	9.9846	2933.85	-38.70		262	333		
332	C6HF5	pentafluorobenzene	1	-7.79730	1.35271	-3.50409	-3.76856	322	TC		
333	C6HF5O	pentafluorophenol	1	-8.69734	2.03071	-5.32619	-3.28915	379	TC		
334	C6H2F4	1,2,3,4-tetrafluorobenzene	1	-7.71223	1.48262	-3.55699	-2.83189	301	TC		
335	C6H2F4	1,2,3,5-tetrafluorobenzene	1	-7.71193	1.46356	-3.49452	-3.04916	288	TC		
336	C6H2F4	1,2,4,5-tetrafluorobenzene	1	-7.79740	1.57406	-3.82060	-2.45398	294	TC		
337	C6H4Cl2	o-dichlorobenzene	1	-8.23991	6.34949	-13.24326	17.25417	403	TC	1.306	293
338	C6H4F2	1,4-difluorobenzene									
339	C6H5Br	bromobenzene	1	-7.54985	2.09359	-3.57864	-1.82558	329	TC	1.495	293
340	C6H5Cl	chlorobenzene	1	-7.58700	2.26551	-4.09418	0.17038	335	TC	1.106	293
341	C6H5F	fluorobenzene	2	48.521	5819.21	-5.489	2910.	300	TC	1.024	293
342	C6H5I	iodobenzene	2	51.071	7589.50	-5.646	4845.	380	TC	1.855	277
343	C6H6	benzene	1	-6.98273	1.33213	-2.62863	-3.33399	288	TC	0.885	289
344	C6H6O	phenol	1	-8.75550	2.92651	-6.31601	-1.36889	380	TC	1.059	313
345	C6H7N	aniline	1	-7.65517	0.85386	-2.51602	-5.96795	376	TC	1.022	293
346	C6H7N	2-methylpyridine	3	9.5725	3259.83	-61.58		352	442	0.950	288
347	C6H7N	3-methylpyridine	3	9.6136	3411.91	-61.95		347	458	0.961	288
348	C6H7N	4-methyl pyridine	1	-7.13732	0.93444	-2.93708	-2.65045	348	TC	0.955	293
349	C6H10	1,5-hexadiene	1	-7.72848	2.21648	-2.23190	-8.51382	273	TC	0.692	293
350	C6H10	cyclohexene	3	9.2041	2813.53	-49.98		300	360	0.816	289

No	Formula	Name	MolWt	Tfp K	Tb K	Tc K	Pc bar	Vc cm³/mol	Zc	Omega	Dipm debye
351	C6H10O	cyclohexanone	98.145	242.0	428.8	629.	39.				3.1
352	C6H11N	capronitrile	97.161	194.	436.8	622.	32.5			0.524	3.5
353	C6H12	cyclohexane	84.162	279.6	353.8	553.5	40.7	308.	0.273	0.212	0.3
354	C6H12	methylcyclopentane	84.162	130.7	345.0	532.7	37.8	319.	0.272	0.231	0.0
355	C6H12	1-hexene	84.163	133.3	336.6	504.0	31.7	350.	0.26	0.285	0.4
356	C6H12	2-hexene,cis	84.162	132.0	342.0	518.	32.8	351.	0.27	0.256	
357	C6H12	2-hexene,trans	84.162	140.	341.0	516.	32.7	351.	0.27	0.242	
358	C6H12	3-hexene,cis	84.162	135.3	339.6	517.	32.8	350.	0.27	0.225	0.3
359	C6H12	3-hexene,trans	84.162	159.7	340.3	519.9	32.5	350.	0.26	0.227	0.0
360	C6H12	2-methyl-2-pentene	84.162	138.1	340.5	518.	32.8	351.	0.27	0.229	
361	C6H12	3-methyl-2-pentene,cis	84.162	138.3	340.9	518.	32.8	351.	0.27	0.269	
362	C6H12	3-methyl-2-pentene,trans	84.162	134.7	343.6	521.	32.9	350.	0.27	0.207	
363	C6H12	4-methyl-2-pentene,cis	84.162	139.	329.6	490.	30.4	360.	0.27	0.29	
364	C6H12	4-methyl-2-pentene,trans	84.162	132.	331.7	493.	30.4	360.	0.27	0.29	
365	C6H12	2,3-dimethyl-1-butene	84.162	115.9	328.8	501.	32.4	343.	0.27	0.221	
366	C6H12	2,3-dimethyl-2-butene	84.162	198.9	346.4	524.	33.6	351.	0.27	0.239	
367	C6H12	3,3-dimethyl-1-butene	84.162	158.	314.4	490.	32.5	340.	0.27	0.121	
368	C6H12O	cyclohexanol	100.160	298.	434.3	625.	37.5			0.528	1.7
369	C6H12O	ethyl propyl ketone	100.160	216.	396.6	582.8	33.2			0.378	
370	C6H12O	methyl butyl ketone	100.160		400.7	587.0	33.2			0.392	
371	C6H12O	methyl isobutyl ketone	100.160	189.	389.6	571.	32.7	400.	0.26	0.385	2.8
372	C6H12O2	n-butyl acetate	116.160	199.7	399.3	579.	31.4	414.	0.267	0.417	1.8
373	C6H12O2	isobutyl acetate	116.160	174.3	389.7	564.	30.2	421.	0.263	0.455	1.9
374	C6H12O2	ethyl butyrate	116.160	180.	394.7	569.	29.6	421.	0.263	0.461	1.8
375	C6H12O2	ethyl isobutyrate	116.160	185.	383.2	555.	29.7	421.	0.271	0.431	2.1

No	Formula	Name	CPVAP A	CPVAP B	CPVAP C	CPVAP D	DELHF	DELGF
351	C6H10O	cyclohexanone	-3.781E+1	5.539E-1	-1.953E-4	-1.534E-8	-2.303E+5	-9.081E+4
352	C6H11N	capronitrile						
353	C6H12	cyclohexane	-5.454E+1	6.113E-1	-2.523E-4	1.321E-8	-1.232E+5	3.178E+4
354	C6H12	methylcyclopentane	-5.011E+1	6.381E-1	-3.642E-4	8.014E-8	-1.068E+5	3.580E+4
355	C6H12	1-hexene	-1.746E+0	5.309E-1	-2.903E-4	6.054E-8	-4.170E+4	8.750E+4
356	C6H12	2-hexene,cis	-9.810E+0	5.309E-1	-2.717E-4	4.827E-8	-5.238E+4	7.628E+4
357	C6H12	2-hexene,trans	-3.292E+1	6.929E-1	-5.619E-4	2.005E-7	-5.393E+4	7.649E+4
358	C6H12	3-hexene,cis	-2.173E+1	5.811E-1	-3.362E-4	7.457E-8	-4.765E+4	8.307E+4
359	C6H12	3-hexene,trans	-4.338E+0	5.510E-1	-3.282E-4	8.047E-8	-5.447E+4	7.767E+4
360	C6H12	2-methyl-2-pentene	-1.475E+1	5.669E-1	-3.341E-4	7.963E-8	-6.653E+4	7.126E+4
361	C6H12	3-methyl-2-pentene,cis	-1.475E+1	5.669E-1	-3.341E-4	7.963E-8	-6.222E+4	7.327E+4
362	C6H12	3-methyl-2-pentene,trans	-1.475E+1	5.669E-1	-3.341E-4	7.963E-8	-6.314E+4	7.134E+4
363	C6H12	4-methyl-2-pentene,cis	-1.675E+0	5.376E-1	-3.044E-4	6.753E-8	-5.748E+4	8.219E+4
364	C6H12	4-methyl-2-pentene,trans	1.263E+1	5.154E-1	-3.007E-4	7.327E-8	-6.150E+4	7.967E+4
365	C6H12	2,3-dimethyl-1-butene	7.025E+0	5.585E-1	-3.696E-4	1.063E-7	-6.636E+4	7.909E+4
366	C6H12	2,3-dimethyl-2-butene	2.294E+0	4.827E-1	-2.199E-4	3.042E-8	-6.984E+4	7.591E+4
367	C6H12	3,3-dimethyl-1-butene	-1.256E+1	5.485E-1	-2.915E-4	5.208E-8	-6.155E+4	9.822E+4
368	C6H12O	cyclohexanol	-5.553E+1	7.214E-1	-4.086E-4	8.235E-8	-2.948E+5	-1.180E+5
369	C6H12O	ethyl propyl ketone						
370	C6H12O	methyl butyl ketone						
371	C6H12O	methyl isobutyl ketone	3.894E+0	5.656E-1	-3.318E-4	8.231E-8	-2.840E+5	
372	C6H12O2	n-butyl acetate	1.362E+1	5.489E-1	-2.278E-4	0.791E-9	-4.868E+5	
373	C6H12O2	isobutyl acetate	7.310E+0	5.740E-1	-2.576E-4	1.101E-8	-4.955E+5	
374	C6H12O2	ethyl butyrate	2.151E+1	4.928E-1	-1.938E-4	3.559E-9		
375	C6H12O2	ethyl isobutyrate						

No	Formula	Name	Eq.	VP A	VP B	VP C	VP D	Tmin	Tmax	LDEN	TDEN
351	C6H100	cyclohexanone	3	9.7814	3677.63	-60.40		363	438	0.951	288
352	C6H11N	capronitrile	1	-6.96009	1.31328	-2.75683	-2.45491	293	TC	0.809	288
353	C6H12	cyclohexane	1	-7.15937	1.48017	-2.92482	-1.98377	288	TC	0.779	293
354	C6H12	methylcyclopentane	1	-7.76467	2.29843	-4.44302	0.89947	289	TC	0.754	289
355	C6H12	1-hexene								0.673	293
356	C6H12	2-hexene,cis	3	9.5855	2897.97	-39.30		245	370	0.687	293
357	C6H12	2-hexene,trans	2	53.818	5734.51	-6.348	3548.	280	TC	0.678	293
358	C6H12	3-hexene,cis	3	9.2182	2680.52	-48.40		245	365	0.680	293
359	C6H12	3-hexene,trans	3	9.3086	2718.68	-47.77		245	365	0.677	293
360	C6H12	2-methyl-2-pentene	3	9.3221	2725.89	-47.64		245	370	0.691	289
361	C6H12	3-methyl-2-pentene,cis	3	9.2922	2731.79	-46.47		248	364	0.694	293
362	C6H12	3-methyl-2-pentene,trans	3	9.3282	2750.50	-48.33		250	366	0.698	293
363	C6H12	4-methyl-2-pentene,cis	3	9.1325	2580.52	-46.56		238	352	0.669	293
364	C6H12	4-methyl-2-pentene,trans	3	9.2223	2631.57	-46.00		240	354	0.669	293
365	C6H12	2,3-dimethyl-1-butene	3	9.1810	2612.69	-43.78		235	360	0.678	293
366	C6H12	2,3-dimethyl-2-butene	1	-7.15852	1.36868	-4.12890	1.53046	302	TC	0.708	293
367	C6H12	3,3-dimethyl-1-butene	1	-6.54633	1.50412	-4.54855	2.96466	264	TC	0.653	293
368	C6H120	cyclohexanol	1	-8.77758	3.11622	-12.3555	7.50610	367	TC	0.942	303
369	C6H120	ethyl propyl ketone	3	9.5000	3144.85	-65.19		347	408	0.813	295
370	C6H120	methyl butyl ketone								0.816	288
371	C6H120	methyl isobutyl ketone	1	-8.54349	2.92801	-5.27311	-2.54507	295	TC	0.801	293
372	C6H1202	n-butyl acetate	1	-8.36658	2.40985	-6.42511	4.85939	333	TC	0.898	273
373	C6H1202	isobutyl acetate	1	-8.12456	1.66934	-4.20511	-3.72813	290	TC	0.875	293
374	C6H1202	ethyl butyrate	1	-8.00073	1.34045	-3.99843	-3.74347	290	TC	0.879	293
375	C6H1202	ethyl isobutyrate	1	-8.08582	1.61436	-4.14816	-3.80720	280	TC	0.869	293

No	Formula	Name	MolWt	Tfp K	Tb K	Tc K	Pc bar	Vc cm³/mol	Zc	Omega	Dipm debye
376	C6H12O2	n-propyl propionate	116.160	197.3	395.8	571.	30.2				1.8
377	C6H12O2	n-amyl formate	116.160	199.7	403.6	576.	34.6			0.538	
378	C6H12O2	isoamyl formate	116.160		396.7	578.					
379	C6H14	n-hexane	86.178	177.8	341.9	507.5	30.1	370.	0.264	0.299	0.0
380	C6H14	2-methyl pentane	86.178	119.5	333.4	497.5	30.1	367.	0.267	0.278	
381	C6H14	3-methyl pentane	86.178	155.	336.4	504.5	31.2	367.	0.273	0.272	
382	C6H14	2,2-dimethyl butane	86.178	173.3	322.8	488.8	30.8	359.	0.272	0.232	
383	C6H14	2,3-dimethyl butane	86.178	144.6	331.1	500.0	31.3	358.	0.269	0.247	
384	C6H14O	1-hexanol	102.177	229.2	430.2	611.	40.5	381.	0.300	0.560	1.8
385	C6H14O	2-hexanol	102.177		411.	586.2					
386	C6H14O	ethyl butyl ether	102.177	170.	365.4	531.	30.4	390.	0.27	0.40	1.2
387	C6H14O	methyl amyl ether	102.177		372.	546.5	30.4	392.	0.262	0.347	
388	C6H14O	dipropyl ether	102.177	151.	363.2	530.6	30.3			0.369	1.2
389	C6H14O	diisopropyl ether	102.177	187.7	341.7	500.3	28.8	386.	0.262	0.331	1.2
390	C6H15N	dipropylamine	101.193	233.6	382.5	555.8	29.9			0.471	1.0
391	C6H15N	diisopropylamine	101.193	212.2	357.1	523.1	30.2	389.	0.265	0.360	1.0
392	C6H15N	triethylamine	101.193	158.4	362.5	535.	30.3	428.	0.260	0.320	0.9
393	C7F8	perfluorotoluene	236.061		377.7	534.5	27.1			0.475	
394	C7F14	perfluoromethylcyclohexane	350.055		349.5	486.8	23.3			0.491	
395	C7F16	perfluoro-n-heptane	388.051	195.	355.6	474.8	16.2	664.	0.273	0.556	
396	C7H3F5	2,3,4,5,6-pentafluorotoluene	182.091		390.7	566.5	31.3	384.	0.255	0.415	
397	C7H5N	benzonitrile	103.124	260.	464.3	699.4	42.2			0.362	3.5
398	C7H6O	benzaldehyde	106.124	216.	452.2	694.8	45.4			0.316	2.8
399	C7H6O2	benzoic acid	122.124	395.6	523.	752.	45.6	341.	0.25	0.62	1.7
400	C7H8	toluene	92.141	178.	383.8	591.8	41.0	316.	0.263	0.263	0.4

No	Formula	Name	CPVAP A	CPVAP B	CPVAP C	CPVAP D	DELHF	DELGF
376	C6H12O2	n-propyl propionate						
377	C6H12O2	n-amyl formate						
378	C6H12O2	isoamyl formate						
379	C6H14	n-hexane	-4.413E+0	5.820E-1	-3.119E-4	6.494E-8	-1.673E+5	-1.670E+2
380	C6H14	2-methyl pentane	-1.057E+1	6.184E-1	-3.573E-4	8.085E-8	-1.744E+5	-5.020E+3
381	C6H14	3-methyl pentane	-2.386E+0	5.690E-1	-2.870E-4	5.033E-8	-1.717E+5	-2.140E+3
382	C6H14	2,2-dimethyl butane	-1.663E+1	6.293E-1	-3.481E-4	6.850E-8	-1.857E+5	-9.630E+3
383	C6H14	2,3-dimethyl butane	-1.461E+1	6.150E-1	-3.376E-4	6.820E-8	-1.779E+5	-4.100E+3
384	C6H14O	1-hexanol	4.811E+0	5.891E-1	-3.010E-4	5.426E-8	-3.178E+5	-1.357E+5
385	C6H14O	2-hexanol						
386	C6H14O	ethyl butyl ether	2.363E+1	5.367E-1	-2.528E-4	4.157E-8		
387	C6H14O	methyl amyl ether						
388	C6H14O	dipropyl ether	1.862E+1	5.335E-1	-2.285E-4	2.442E-8	-2.931E+5	-1.056E+5
389	C6H14O	diisopropyl ether	7.505E+0	5.849E-1	-3.027E-4	5.845E-8	-3.190E+5	-1.220E+5
390	C6H15N	dipropylamine	6.460E+0	6.293E-1	-3.390E-4	7.072E-8		
391	C6H15N	diisopropylamine						
392	C6H15N	triethylamine	-1.843E+1	7.155E-1	-4.392E-4	1.092E-7	-9.965E+4	1.104E+5
393	C7F8	perfluorotoluene						
394	C7F14	perfluoromethylcyclohexane					-2.898E+6	
395	C7F16	perfluoro-n-heptane					-3.387E+6	-3.089E+6
396	C7H3F5	2,3,4,5,6-pentafluorotoluene						
397	C7H5N	benzonitrile	-2.605E+1	5.732E-1	-4.430E-4	1.349E-7	2.190E+5	2.610E+5
398	C7H6O	benzaldehyde	-1.214E+1	4.961E-1	-2.845E-4	5.167E-8	-3.680E+4	2.240E+4
399	C7H6O2	benzoic acid	-5.129E+1	6.293E-1	-4.237E-4	1.062E-7	-2.904E+5	-2.106E+5
400	C7H8	toluene	-2.435E+1	5.125E-1	-2.765E-4	4.911E-8	5.003E+4	1.221E+5

No	Formula	Name	Eq.	VP A	VP B	VP C	VP D	Tmin	Tmax	LDEN	TDEN
376	C6H12O2	n-propyl propionate	1	-8.00913	1.33297	-3.97513	-3.83674	290	TC	0.881	293
377	C6H12O2	n-amyl formate								0.902	273
378	C6H12O2	isoamyl formate								0.882	293
379	C6H14	n-hexane	1	-7.46765	1.44211	-3.28222	-2.50941	220	TC	0.659	293
380	C6H14	isohexane	1	-7.31728	1.33940	-3.06807	-1.99255	240	TC	0.653	293
381	C6H14	3-methyl pentane	1	-7.27084	1.26113	-2.81741	-2.17642	235	TC	0.664	293
382	C6H14	2,2-dimethyl butane	1	-7.24296	1.66876	-3.23718	-0.53171	225	TC	0.649	293
383	C6H14	2,3-dimethyl butane	1	-7.27870	1.56349	-3.05387	-1.57752	235	TC	0.662	293
384	C6H14O	1-hexanol	3	11.4792	4055.45	-76.49		308	430	0.819	293
385	C6H14O	2-hexanol	3	10.0989	3158.53	-99.98		295	418	0.816	293
386	C6H14O	ethyl butyl ether	1	-8.30292	2.02889	-3.26245	-6.32274	311	TC	0.749	293
387	C6H14O	methyl amyl ether								0.75	298
388	C6H14O	dipropyl ether	1	-8.22229	2.22110	-3.90291	-3.77431	288	TC	0.736	293
389	C6H14O	diisopropyl ether	1	-7.62613	1.29308	-2.90101	-6.14467	297	TC	0.724	293
390	C6H15N	dipropylamine	1	-8.56471	2.93461	-5.56089	0.56571	275	TC	0.738	293
391	C6H15N	diisopropylamine	1	-7.84319	1.80097	-4.66547	-0.29364	257	TC	0.722	295
392	C6H15N	triethylamine	1	-11.3617	10.0092	-13.4750	-9.36035	323	TC	0.728	293
393	C7F8	perfluorotoluene									
394	C7F14	perfluoromethylcyclohexane	1	-10.5469	6.38028	-10.6940	11.6006	306	TC	1.789	298
395	C7F16	perfluoro-n-heptane	1	-9.13392	2.75328	-8.33813	6.82085	271	TC	1.733	293
396	C7H3F5	2,3,4,5,6-pentafluorotoluene	1	-8.05688	1.46673	-3.82439	-2.78727	313	TC	1.010	288
397	C7H5N	benzonitrile	2	53.154	7912.31	-5.881	4898.	340	TC	1.045	293
398	C7H6O	benzaldehyde	1	-7.16527	0.52710	-1.51484	-7.92908	300	TC	1.075	293
399	C7H6O2	benzoic acid	3	10.5432	4190.70	-125.2		405	560	1.075	403
400	C7H8	toluene	1	-7.28607	1.38091	-2.83433	-2.79168	309	TC	0.867	293

No	Formula	Name	MolWt	Tfp K	Tb K	Tc K	Pc bar	Vc cm^3/mol	Zc	Omega	Dipm debye
401	C7H8O	methyl phenyl ether	108.140	235.7	426.8	645.6	42.5			0.347	1.2
402	C7H8O	benzyl alcohol	108.140	257.8	478.6	720.2	44.0				1.7
403	C7H8O	o-cresol	108.140	304.1	464.2	697.6	50.1			0.433	1.6
404	C7H8O	m-cresol	108.140	285.4	475.4	705.8	45.6	309.	0.240	0.454	1.8
405	C7H8O	p-cresol	108.140	307.9	475.1	704.6	51.5			0.505	1.6
406	C7H9N	2,3-dimethylpyridine	107.156		434.4	655.4					2.2
407	C7H9N	2,4-dimethylpyridine	107.156		431.6	647.					2.3
408	C7H9N	2,5-dimethylpyridine	107.156		430.2	644.2					2.2
409	C7H9N	2,6-dimethylpyridine	107.156	267.	417.2	623.8					1.7
410	C7H9N	3,4-dimethylpyridine	107.156		452.3	683.8					1.9
411	C7H9N	3,5-dimethylpyridine	107.156		445.1	667.2					2.6
412	C7H9N	N-methylaniline	107.156	216.	469.4	701.	52.0			0.475	1.7
413	C7H9N	o-toluidine	107.156	258.4	473.5	694.	37.5			0.438	1.6
414	C7H9N	m-toluidine	107.156	242.8	476.6	709.	41.5			0.410	1.5
415	C7H9N	p-toluidine	107.156	316.9	473.7	667.	23.8			0.443	1.6
416	C7H14	cycloheptane	98.189	265.	391.6	604.2	38.1	353.	0.268	0.237	
417	C7H14	1,1-dimethylcyclopentane	98.189	203.4	361.0	547.	34.4	360.	0.27	0.273	
418	C7H14	1,2-dimethylcyclopentane-cis	98.189	219.3	372.7	564.8	34.4	368.	0.27	0.269	
419	C7H14	1,2-dimethylcyclopentane-trans	98.189	155.6	365.0	553.2	34.4	362.	0.27	0.269	
420	C7H14	ethylcyclopentane	98.189	134.7	376.6	569.5	34.0	375.	0.269	0.271	
421	C7H14	methylcyclohexane	98.189	146.6	374.1	572.2	34.7	368.	0.268	0.236	0.0
422	C7H14	1-heptene	98.189	154.3	366.8	537.3	28.3	440.	0.28	0.358	0.3
423	C7H14	2,3,3-trimethyl-1-butene	98.189	163.3	351.0	533.	28.9	400.	0.26	0.192	
424	C7H140	methyl amyl ketone	114.188		424.2	611.5	34.4			0.483	
425	C7H1402	n-propyl butyrate	130.187	176.0	416.2	590.	27.1				1.8

No	Formula	Name	CPVAP A	CPVAP B	CPVAP C	CPVAP D	DELHF	DELGF
401	C7H80	methyl phenyl ether	-7.398E+0	5.481E-1	-3.357E-4	7.771E-8	-9.408E+4	
402	C7H80	benzyl alcohol					-1.287E+5	-3.300E+4
403	C7H80	o-cresol	-3.228E+1	7.005E-1	-5.924E-4	2.124E-7	-1.324E+5	-4.057E+4
404	C7H80	m-cresol	-4.501E+1	7.264E-1	-6.029E-4	2.077E-7	-1.255E+5	-3.090E+4
405	C7H80	p-cresol	-4.063E+1	7.055E-1	-5.757E-4	1.967E-7		
406	C7H9N	2,3-dimethylpyridine					6.829E+4	
407	C7H9N	2,4-dimethylpyridine						
408	C7H9N	2,5-dimethylpyridine					6.644E+4	
409	C7H9N	2,6-dimethylpyridine						
410	C7H9N	3,4-dimethylpyridine					7.005E+4	
411	C7H9N	3,5-dimethylpyridine					7.281E+4	1.993E+5
412	C7H9N	N-methylaniline					8.541E+4	
413	C7H9N	o-toluidine						
414	C7H9N	m-toluidine	-1.599E+1	5.681E-1	-3.033E-4	4.643E-8		
415	C7H9N	p-toluidine						
416	C7H14	cycloheptane	-7.619E+1	7.867E-1	-4.204E-4	7.561E-8	-1.194E+5	6.305E+4
417	C7H14	1,1-dimethylcyclopentane	-5.789E+1	7.670E-1	-4.501E-4	1.010E-7	-1.384E+5	3.906E+4
418	C7H14	1,2-dimethylcyclopentane-cis	-5.564E+1	7.616E-1	-4.484E-4	1.014E-7	-1.296E+5	4.576E+4
419	C7H14	1,2-dimethylcyclopentane-trans	-5.452E+1	7.591E-1	-4.480E-4	1.017E-7	-1.368E+5	3.839E+4
420	C7H14	ethylcyclopentane	-5.531E+1	7.511E-1	-4.396E-4	1.004E-7	-1.272E+5	4.459E+4
421	C7H14	methylcyclohexane	-6.192E+1	7.842E-1	-4.438E-4	9.366E-8	-1.549E+5	2.730E+4
422	C7H14	1-heptene	-3.303E+0	6.297E-1	-3.512E-4	7.607E-8	-6.234E+4	9.588E+4
423	C7H14	2,3,3-trimethyl-1-butene					-8.654E+4	
424	C7H140	methyl amyl ketone						
425	C7H1402	n-propyl butyrate						

No	Formula	Name	Eq.	VP A	VP B	VP C	VP D	Tmin	Tmax	LDEN	TDEN
401	C7H8O	methyl phenyl ether	1	-7.87545	1.83291	-4.06977	-2.18906	357	TC	0.996	293
402	C7H8O	benzyl alcohol	1	-7.09506	1.18389	-9.14255	5.56311	303	TC	1.041	298
403	C7H8O	o-cresol	1	-8.82061	3.14917	-6.63041	-0.84857	393	TC	1.028	313
404	C7H8O	m-cresol	1	-8.58506	2.82624	-8.57418	8.74822	423	TC	1.034	293
405	C7H8O	p-cresol	1	-9.23951	3.29880	-7.17725	-0.48000	401	TC	1.019	313
406	C7H9N	2,3-dimethylpyridine	3	10.5290	4219.74	-33.04		420	440	0.942	298
407	C7H9N	2,4-dimethylpyridine	3	10.2785	3991.27	-42.79		418	438	0.949	273
408	C7H9N	2,5-dimethylpyridine	3	9.6844	3545.14	-63.59		350	435	0.938	273
409	C7H9N	2,6-dimethylpyridine	3	9.6286	3385.20	-65.19		350	420	0.923	298
410	C7H9N	3,4-dimethylpyridine	3	10.3315	4237.04	-41.65		400	460	0.954	298
411	C7H9N	3,5-dimethylpyridine	3	10.2648	4106.95	-44.45		400	460	0.939	298
412	C7H9N	N-methylaniline	3	9.6864	3756.28	-80.71		320	480	0.989	293
413	C7H9N	o-toluidine	1	-8.68458	2.72553	-5.94620	-1.09185	392	TC	0.998	293
414	C7H9N	m-toluidine	1	-8.43741	2.58101	-6.00776	-1.52856	395	TC	0.989	293
415	C7H9N	p-toluidine	3	10.0766	4041.04	-72.15		350	500	0.964	323
416	C7H14	cycloheptane	3	9.1616	3066.05	-56.80		330	435	0.810	293
417	C7H14	1,1-dimethylcyclopentane	1	-7.56029	1.82906	-2.90303	-3.11433	289	TC	0.759	289
418	C7H14	1,2-dimethylcyclopentane-cis	1	-7.67242	2.20160	-3.86394	-1.16796	299	TC	0.777	289
419	C7H14	1,2-dimethylcyclopentane-trans	1	-7.19675	1.03696	-1.93618	-5.30531	299	TC	0.756	289
420	C7H14	ethylcyclopentane	1	-7.68089	2.28014	-4.40365	0.54338	302	TC	0.771	289
421	C7H14	methylcyclohexane	1	-7.01915	1.09615	-2.37009	-3.37562	299	TC	0.774	289
422	C7H14	1-heptene	1	-8.26875	3.02688	-6.18709	4.33049	295	TC	0.697	293
423	C7H14	2,3,3-trimethyl-1-butene	3	9.0334	2719.47	-49.56		253	375	0.705	293
424	C7H14O	methyl amyl ketone								0.820	288
425	C7H14O2	n-propyl butyrate	1	-8.28062	1.40511	-4.19323	-3.70158	300	TC	0.879	288

No	Formula	Name	MolWt	Tfp K	Tb K	Tc K	Pc bar	Vc cm³/mol	Zc	Omega	Dipm debye
426	C7H14O2	n-propyl isobutyrate	130.187		408.6	581.	28.3				
427	C7H14O2	isoamyl acetate	130.187	194.7	415.7	599.					1.8
428	C7H14O2	isobutyl propionate	130.187	201.8	410.0	583.	27.7				
429	C7H16	n-heptane	100.205	182.6	371.6	540.3	27.4	432.	0.263	0.349	0.0
430	C7H16	2-methylhexane	100.205	154.9	363.2	530.4	27.3	421.	0.261	0.329	0.0
431	C7H16	3-methylhexane	100.205	100.0	365.0	535.3	28.1	404.	0.255	0.323	0.0
432	C7H16	2,2-dimethylpentane	100.205	149.4	352.4	520.5	27.7	416.	0.266	0.287	0.0
433	C7H16	2,3-dimethylpentane	100.205		362.9	537.4	29.1	393.	0.256	0.296	0.0
434	C7H16	2,4-dimethylpentane	100.205	154.	353.6	519.8	27.4	418.	0.264	0.302	0.0
435	C7H16	3,3-dimethylpentane	100.205	138.7	359.2	536.4	29.5	414.	0.273	0.267	0.0
436	C7H16	3-ethylpentane	100.205	154.6	366.6	540.6	28.9	416.	0.267	0.310	0.0
437	C7H16	2,2,3-trimethylbutane	100.205	248.3	354.0	531.2	29.5	398.	0.266	0.250	0.0
438	C7H16O	1-heptanol	116.204	239.2	449.8	633.	30.4	435.	0.251	0.560	1.7
439	C8H4O3	phthalic anhydride	148.118	404.	560.	810.	47.6	368.	0.26		5.3
440	C8H8	styrene	104.152	242.5	418.3	647.	39.9			0.257	0.1
441	C8H8O	methyl phenyl ketone	120.151	292.8	474.9	714.0	40.6	376.	0.257	0.42	3.0
442	C8H8O2	methyl benzoate	136.151	260.8	472.2	692.	36.4	396.	0.25	0.43	1.9
443	C8H8O3	methyl salicylate	152.149	264.6	496.1	709.					2.4
444	C8H10	o-xylene	106.168	248.0	417.6	630.3	37.3	369.	0.262	0.310	0.5
445	C8H10	m-xylene	106.168	225.3	412.3	617.1	35.4	376.	0.259	0.325	0.3
446	C8H10	p-xylene	106.168	286.4	411.5	616.2	35.1	379.	0.260	0.320	0.1
447	C8H10	ethylbenzene	106.168	178.2	409.3	617.2	36.0	374.	0.262	0.302	0.4
448	C8H10O	o-ethylphenol	122.167	269.8	477.7	703.0					
449	C8H10O	m-ethylphenol	122.167	269.	491.6	718.8					
450	C8H10O	p-ethylphenol	122.167	318.	491.1	716.4					

No	Formula	Name	CPVAP A	CPVAP B	CPVAP C	CPVAP D	DELHF	DELGF
426	C7H14O2	n-propyl isobutyrate						
427	C7H14O2	isoamyl acetate						
428	C7H14O2	isobutyl propionate						
429	C7H16	n-heptane	-5.146E+0	6.762E-1	-3.651E-4	7.658E-8	-1.879E+5	8.000E+3
430	C7H16	2-methylhexane	-3.939E+1	8.642E-1	-6.289E-4	1.836E-7	-1.951E+5	3.220E+3
431	C7H16	3-methylhexane	-7.046E+0	6.837E-1	-3.734E-4	7.834E-8	-1.924E+5	4.600E+3
432	C7H16	2,2-dimethylpentane	-5.010E+1	8.956E-1	-6.360E-4	1.736E-7	-2.063E+5	8.400E+2
433	C7H16	2,3-dimethylpentane	-7.046E+0	6.837E-1	-3.734E-4	7.834E-8	-1.994E+5	6.700E+2
434	C7H16	2,4-dimethylpentane	-7.046E+0	6.837E-1	-3.734E-4	7.834E-8	-2.021E+5	3.100E+3
435	C7H16	3,3-dimethylpentane	-7.046E+0	6.837E-1	-3.734E-4	7.834E-8	-2.017E+5	2.640E+3
436	C7H16	3-ethylpentane	-7.046E+0	6.837E-1	-3.734E-4	7.834E-8	-1.898E+5	1.100E+4
437	C7H16	2,2,3-trimethylbutane	-2.294E+1	7.519E-1	-4.421E-4	1.005E-7	-2.049E+5	4.270E+3
438	C7H16O	1-heptanol	4.907E+1	6.778E-1	-3.447E-4	6.046E-8	-3.320E+5	-1.210E+5
439	C8H4O3	phthalic anhydride	-4.455E+0	6.540E-1	-4.283E-4	1.009E-7	-3.718E+5	
440	C8H8	styrene	-2.825E+1	6.159E-1	-4.023E-4	9.935E-8	1.475E+5	2.139E+5
441	C8H8O	methyl phenyl ketone	-2.958E+1	6.410E-1	-4.071E-4	9.722E-8	-8.692E+4	1.840E+3
442	C8H8O2	methyl benzoate	-2.121E+1	5.501E-1	-1.799E-4	4.425E-8	-2.541E+5	
443	C8H8O3	methyl salicylate						
444	C8H10	o-xylene	-1.585E+1	5.962E-1	-3.443E-4	7.528E-8	1.900E+4	1.222E+5
445	C8H10	m-xylene	-2.917E+1	6.297E-1	-3.747E-4	8.478E-8	1.725E+4	1.189E+5
446	C8H10	p-xylene	-2.509E+1	6.042E-1	-3.374E-4	6.820E-8	1.796E+4	1.212E+5
447	C8H10	ethylbenzene	-4.310E+1	7.072E-1	-4.811E-4	1.301E-7	2.981E+4	1.307E+5
448	C8H10O	o-ethylphenol					-1.458E+5	
449	C8H10O	m-ethylphenol					-1.466E+5	
450	C8H10O	p-ethylphenol					-1.447E+5	

No	Formula	Name	Eq.	VP A	VP B	VP C	VP D	Tmin	Tmax	LDEN	TDEN
426	C7H14O2	n-propyl isobutyrate	1	-8.52052	2.10660	-4.44053	-3.90420	300	TC	0.884	273
427	C7H14O2	isoamyl acetate	3	10.5011	3699.29	-57.54		311	369	0.876	288
428	C7H14O2	isobutyl propionate	1	-8.32761	1.56574	-3.97739	-4.71845	300	TC	0.888	273
429	C7H16	n-heptane	1	-7.67468	1.37068	-3.53620	-3.20243	240	TC	0.684	293
430	C7H16	2-methylhexane	1	-7.62477	1.47806	-3.53616	-2.70794	230	TC	0.679	293
431	C7H16	3-methylhexane	1	-7.58592	1.47394	-3.52511	-2.35419	235	TC	0.687	293
432	C7H16	2,2-dimethylpentane	1	-7.45564	1.56232	-3.44620	-1.80802	225	TC	0.674	293
433	C7H16	2,3-dimethylpentane	1	-7.46078	1.47778	-3.37079	-1.88997	230	TC	0.695	293
434	C7H16	2,4-dimethylpentane	1	-7.46358	1.43203	-3.42422	-2.20238	225	TC	0.673	293
435	C7H16	3,3-dimethylpentane	1	-7.49199	1.83146	-3.57292	-0.89448	225	TC	0.693	293
436	C7H16	3-ethylpentane	1	-7.58305	1.58587	-3.56732	-2.42625	265	TC	0.698	293
437	C7H16	2,2,3-trimethylbutane	1	-7.22017	1.44914	-3.11808	-1.10598	250	TC	0.690	293
438	C7H16O	1-heptanol	3	8.6866	2626.42	-146.6		333	449	0.822	293
439	C8H4O3	phthalic anhydride	3	9.3782	4467.01	-83.15		409	615		
440	C8H8	styrene	1	-7.15981	1.78861	-5.10359	1.63749	303	TC	0.906	293
441	C8H8O	methyl phenyl ketone	1	-7.63896	1.20432	-3.60753	-1.55754	298	TC	1.032	288
442	C8H8O2	methyl benzoate	3	9.6070	3751.83	-81.15		350	516	1.086	293
443	C8H8O3	methyl salicylate	3	9.6897	3943.86	-86.19		350	495	1.182	298
444	C8H10	o-xylene	1	-7.53357	1.40968	-3.10985	-2.85992	337	TC	0.880	293
445	C8H10	m-xylene	1	-7.59222	1.39441	-3.22746	-2.40376	332	TC	0.864	293
446	C8H10	p-xylene	1	-7.63495	1.50724	-3.19678	-2.78710	331	TC	0.861	293
447	C8H10	ethylbenzene	1	-7.48645	1.45488	-3.37538	-2.23048	330	TC	0.867	293
448	C8H10O	o-ethylphenol	3	11.3408	4928.36	-45.75		350	500	1.037	273
449	C8H10O	m-ethylphenol	3	10.5753	4272.77	-86.08		370	500	1.025	273
450	C8H10O	p-ethylphenol	3	12.4703	5579.62	-44.15		370	500		273

No	Formula	Name	MolWt	Tfp K	Tb K	Tc K	Pc bar	Vc cm³/mol	Zc	Omega	Dipm debye
451	C8H10O	ethyl phenyl ether	122.167	243.	443.0	647.	34.2			0.418	1.2
452	C8H10O	2,3-xylenol	122.167	348.	490.1	722.8					2.0
453	C8H10O	2,4-xylenol	122.167	298.	484.1	707.6					1.5
454	C8H10O	2,5-xylenol	122.167	348.	484.3	706.9					
455	C8H10O	2,6-xylenol	122.167	322.	474.2	701.0					
456	C8H10O	3,4-xylenol	122.167	338.	500.2	729.8					1.7
457	C8H10O	3,5-xylenol	122.167	337.	494.9	715.6					1.8
458	C8H11N	N,N-dimethylaniline	121.183	275.6	467.3	687.	36.3			0.411	1.6
459	C8H11N	N-ethylaniline	121.183	207.4	476.2	698.					1.7
460	C8H14O4	diethylsuccinate	174.196	251.9	490.9	663.					2.3
461	C8H16	1,1-dimethylcyclohexane	112.216	239.7	392.7	591.	29.6	416.	0.25	0.238	
462	C8H16	1,2-dimethylcyclohexane-cis	112.216	223.1	402.9	606.	29.6			0.236	
463	C8H16	1,2-dimethylcyclohexane-trans	112.216	185.0	396.6	596.				0.242	
464	C8H16	1,3-dimethylcyclohexane-cis	112.216	197.6	393.3	591.	29.6			0.224	
465	C8H16	1,3-dimethylcyclohexane-trans	112.216	183.0	397.6	598.	29.7			0.189	
466	C8H16	1,4-dimethylcyclohexane-cis	112.216	185.7	397.5	598.	29.7			0.234	
467	C8H16	1,4-dimethylcyclohexane-trans	112.216		392.5	587.7	29.7			0.242	
468	C8H16	ethylcyclohexane	112.216	161.8	404.9	609.	30.	450.	0.27	0.243	0.0
469	C8H16	1,1,2-trimethylcyclopentane	112.216		386.9	579.5	29.4			0.252	
470	C8H16	1,1,3-trimethylcyclopentane	112.216		378.0	569.5	28.3			0.211	
471	C8H16	1,2,4-trimethylcyclopentane-c,c,t	112.216		391.	579.	29.			0.277	
472	C8H16	1,2,4-trimethylcyclopentane-c,t,c	112.216		382.4	571.	28.			0.246	
473	C8H16	1-methyl-1-ethylcyclopentane	112.216		394.7	592.	30.			0.250	
474	C8H16	n-propylcyclopentane	112.216	155.8	404.1	603.	30.	425.	0.25	0.335	
475	C8H16	isopropylcyclopentane	112.216	160.5	399.6	601.	30.			0.240	

No	Formula	Name	CPVAP A	CPVAP B	CPVAP C	CPVAP D	DELHF	DELGF
451	C8H10O	ethyl phenyl ether						
452	C8H10O	2,3-xylenol					-1.573E+5	
453	C8H10O	2,4-xylenol					-1.628E+5	
454	C8H10O	2,5-xylenol					-1.615E+5	
455	C8H10O	2,6-xylenol					-1.619E+5	
456	C8H10O	3,4-xylenol					-1.565E+5	
457	C8H10O	3,5-xylenol					-1.615E+5	
458	C8H11N	N,N-dimethylaniline					8.415E+4	2.314E+5
459	C8H11N	N-ethylaniline						
460	C8H1404	diethylsuccinate						
461	C8H16	1,1-dimethylcyclohexane	-7.211E+1	8.997E-1	-5.020E-4	1.030E-7	-1.811E+5	3.525E+4
462	C8H16	1,2-dimethylcyclohexane-cis	-6.837E+1	8.972E-1	-5.137E-4	1.099E-7	-1.723E+5	4.124E+4
463	C8H16	1,2-dimethylcyclohexane-trans	-6.848E+1	9.123E-1	-5.355E-4	1.181E-7	-1.801E+5	3.450E+4
464	C8H16	1,3-dimethylcyclohexane-cis	-6.516E+1	8.838E-1	-4.932E-4	1.020E-7	-1.849E+5	2.985E+4
465	C8H16	1,3-dimethylcyclohexane-trans	-6.415E+1	8.826E-1	-5.016E-4	1.068E-7	-1.767E+5	3.634E+4
466	C8H16	1,4-dimethylcyclohexane-cis	-6.415E+1	8.826E-1	-5.016E-4	1.068E-7	-1.768E+5	3.797E+4
467	C8H16	1,4-dimethylcyclohexane-trans	-7.036E+1	9.131E-1	-5.309E-4	1.155E-7	-1.847E+5	3.174E+4
468	C8H16	ethylcyclohexane	-6.389E+1	8.893E-1	-5.108E-4	1.103E-7	-1.719E+5	3.927E+4
469	C8H16	1,1,2-trimethylcyclopentane						
470	C8H16	1,1,3-trimethylcyclopentane						
471	C8H16	1,2,4-trimethylcyclopentane-c,c,t						
472	C8H16	1,2,4-trimethylcyclopentane-c,t,c						
473	C8H16	1-methyl-1-ethylcyclopentane						
474	C8H16	n-propylcyclopentane	-5.597E+1	8.449E-1	-4.924E-4	1.117E-7	-1.482E+5	5.263E+4
475	C8H16	isopropylcyclopentane						

No	Formula	Name	Eq.	VP A	VP B	VP C	VP D	Tmin	Tmax	LDEN	TDEN
451	C8H10O	ethyl phenyl ether	1	-8.50867	2.56997	-5.78999	0.10899	371	TC	0.979	277
452	C8H10O	2,3-xylenol	3	9.6222	3724.58	-102.4		420	500		
453	C8H10O	2,4-xylenol	3	9.6254	3655.26	-103.8		410	500		
454	C8H10O	2,5-xylenol	3	9.6166	3667.32	-102.4		410	490		
455	C8H10O	2,6-xylenol	3	9.6607	3749.35	-85.55		400	480		
456	C8H10O	3,4-xylenol	3	9.6802	3733.53	-113.9		430	520		
457	C8H10O	3,5-xylenol	3	9.7990	3775.91	-109.0		410	500		
458	C8H11N	N,N-dimethylaniline	3	10.3445	4276.08	-52.80		345	480	0.956	293
459	C8H11N	N-ethylaniline	3	10.4715	4382.63	-58.88		321	481	0.963	293
460	C8H14O4	diethyl succinate								1.041	293
461	C8H16	1,1-dimethylcyclohexane	1	-6.92810	1.01872	-3.04857	-1.70684	314	TC	0.785	289
462	C8H16	1,2-dimethylcyclohexane-cis	1	-7.01944	1.31860	-3.96577	0.08142	322	TC	0.796	293
463	C8H16	1,2-dimethylcyclohexane-trans	2	46.903	6162.66	-5.245	4785.	320	TC	0.776	293
464	C8H16	1,3-dimethylcyclohexane-cis	3	9.1268	3081.95	-55.08		284	420	0.766	293
465	C8H16	1,3-dimethylcyclohexane-trans	2	49.477	6271.67	-5.615	4718.	320	TC	0.785	293
466	C8H16	1,4-dimethylcyclohexane-cis	2	46.951	6219.26	-5.233	4718.	320	TC	0.783	293
467	C8H16	1,4-dimethylcyclohexane-trans	2	46.289	6071.72	-5.163	4650.	320	TC	0.763	293
468	C8H16	ethylcyclohexane	3	9.1923	3183.25	-58.15		293	433	0.788	293
469	C8H16	1,1,2-trimethylcyclopentane	1	-7.01985	1.06194	-3.15886	-1.64858	309	TC		
470	C8H16	1,1,3-trimethylcyclopentane	1	-6.97215	1.62353	-4.90587	2.76293	302	TC		
471	C8H16	1,2,4-trimethylcyclopentane-c,c,t	3	9.1341	3073.95	-54.20		283	418		
472	C8H16	1,2,4-trimethylcyclopentane-c,t,c	3	9.1554	3009.70	-53.23		282	417		
473	C8H16	1-methyl-1-ethylcyclopentane	1	-7.09092	1.31715	-3.96332	0.30332	316	TC		
474	C8H16	n-propylcyclopentane	1	-7.82031	2.88785	-6.85367	6.03561	325	TC	0.781	289
475	C8H16	isopropylcyclopentane	1	-7.10096	1.54495	-4.66594	2.34067	320	TC	0.776	293

No	Formula	Name	MolWt	Tfp K	Tb K	Tc K	Pc bar	Vc cm³/mol	Zc	Omega	Dipm debye
476	C8H16	cyclooctane	112.216	287.6	422.	647.2	35.6	410.	0.271	0.236	
477	C8H16	1-octene	112.216	171.4	394.4	566.7	26.2	464.	0.26	0.386	0.3
478	C8H16	2-octene-trans	112.216	185.4	398.1	580.	27.7			0.350	
479	C8H16O2	isoamyl propionate	144.214		433.4	611.					
480	C8H16O2	isobutyl butyrate	144.214		430.1	603.	24.5				
481	C8H16O2	isobutyl isobutyrate	144.214		421.8	594.					
482	C8H16O2	n-propyl isovalerate	144.214		429.1	609.					
483	C8H18	n-octane	114.232	216.4	398.8	568.8	24.9	492.	0.259	0.398	0.0
484	C8H18	2-methylheptane	114.232	164.	390.8	559.6	24.8	488.	0.261	0.378	
485	C8H18	3-methylheptane	114.232	152.7	392.1	563.7	25.5	464.	0.252	0.370	
486	C8H18	4-methylheptane	114.232	152.2	390.9	561.7	25.4	476.	0.259	0.371	
487	C8H18	2,2-dimethylhexane	114.232	152.	380.0	549.9	25.3	478.	0.264	0.338	
488	C8H18	2,3-dimethylhexane	114.232		388.8	563.5	26.3	468.	0.263	0.346	
489	C8H18	2,4-dimethylhexane	114.232		382.6	553.5	25.6	472.	0.262	0.343	
490	C8H18	2,5-dimethylhexane	114.232	181.9	382.3	550.1	24.9	482.	0.262	0.356	
491	C8H18	3,3-dimethylhexane	114.232	147.	385.1	562.0	26.5	443.	0.251	0.320	
492	C8H18	3,4-dimethylhexane	114.232		390.9	568.9	26.9	466.	0.265	0.338	
493	C8H18	3-ethylhexane	114.232		391.7	565.5	26.1	455.	0.252	0.361	
494	C8H18	2,2,3-trimethylpentane	114.232	160.9	383.0	563.5	27.3	436.	0.254	0.297	
495	C8H18	2,2,4-trimethylpentane	114.232	165.8	372.4	544.0	25.7	468.	0.266	0.303	
496	C8H18	2,3,3-trimethylpentane	114.232	172.5	387.9	573.6	28.2	455.	0.269	0.290	
497	C8H18	2,3,4-trimethylpentane	114.232	163.9	386.6	566.4	27.3	461.	0.267	0.315	
498	C8H18	2-methyl-3-ethylpentane	114.232	158.2	388.8	567.1	27.0	443.	0.254	0.330	
499	C8H18	3-methyl-3-ethylpentane	114.232	182.3	391.4	576.6	28.1	455.	0.267	0.303	
500	C8H18	2,2,3,3-tetramethylbutane	114.232	374.	379.6	567.8	28.7	461.	0.280	0.251	

No	Formula	Name	CPVAP A	CPVAP B	CPVAP C	CPVAP D	DELHF	DELGF
476	C8H16	cyclooctane						
477	C8H16	1-octene	-4.099E+0	7.239E-1	-4.036E-4	8.675E-8	-8.298E+4	1.043E+5
478	C8H16	2-octene-trans	-1.282E+1	7.532E-1	-4.442E-4	1.050E-7	-9.458E+4	9.274E+4
479	C8H16O2	isoamyl propionate						
480	C8H16O2	isobutyl butyrate						
481	C8H16O2	isobutyl isobutyrate						
482	C8H16O2	n-propyl isovalerate						
483	C8H18	n-octane	-6.096E+0	7.712E-1	-4.195E-4	8.855E-8	-2.086E+5	1.640E+4
484	C8H18	2-methylheptane	-8.970E+1	1.242E+0	-1.176E-3	4.618E-7	-2.156E+5	1.277E+4
485	C8H18	3-methylheptane	-9.215E+0	7.859E-1	-4.400E-4	9.697E-8	-2.128E+5	1.373E+4
486	C8H18	4-methylheptane	-9.215E+0	7.859E-1	-4.400E-4	9.697E-8	-2.122E+5	1.675E+4
487	C8H18	2,2-dimethylhexane	-9.215E+0	7.859E-1	-4.400E-4	9.697E-8	-2.249E+5	1.072E+4
488	C8H18	2,3-dimethylhexane	-9.215E+0	7.859E-1	-4.400E-4	9.697E-8	-2.141E+5	1.771E+4
489	C8H18	2,4-dimethylhexane	-9.215E+0	7.859E-1	-4.400E-4	9.697E-8	-2.196E+5	1.172E+4
490	C8H18	2,5-dimethylhexane	-9.215E+0	7.859E-1	-4.400E-4	9.697E-8	-2.228E+5	1.047E+4
491	C8H18	3,3-dimethylhexane	-9.215E+0	7.859E-1	-4.400E-4	9.697E-8	-2.203E+5	1.327E+4
492	C8H18	3,4-dimethylhexane	-9.215E+0	7.859E-1	-4.400E-4	9.697E-8	-2.131E+5	1.733E+4
493	C8H18	3-ethylhexane	-9.215E+0	7.859E-1	-4.400E-4	9.697E-8	-2.110E+5	1.694E+4
494	C8H18	2,2,3-trimethylpentane	-9.215E+0	7.859E-1	-4.400E-4	9.697E-8	-2.203E+5	1.712E+4
495	C8H18	2,2,4-trimethylpentane	-7.461E+0	7.779E-1	-4.287E-4	9.173E-8	-2.243E+5	1.369E+4
496	C8H18	2,3,3-trimethylpentane	-9.215E+0	7.859E-1	-4.400E-4	9.697E-8	-2.166E+5	1.892E+4
497	C8H18	2,3,4-trimethylpentane	-9.215E+0	7.859E-1	-4.400E-4	9.697E-8	-2.176E+5	1.892E+4
498	C8H18	2-methyl-3-ethylpentane	-9.215E+0	7.859E-1	-4.400E-4	9.697E-8	-2.113E+5	2.127E+4
499	C8H18	3-methyl-3-ethylpentane	-9.215E+0	7.859E-1	-4.400E-4	9.697E-8	-2.151E+5	1.993E+4
500	C8H18	2,2,3,3-tetramethylbutane						

No	Formula	Name	Eq.	VP A	VP B	VP C	VP D	Tmin	Tmax	LDEN	TDEN
476	C8H16	cyclooctane	3	9.1799	3310.62	-63.18		367	470	0.834	293
477	C8H16	1-octene	2	57.867	6883.34	-6.765	5235.	320	TC	0.715	293
478	C8H16	2-octene-trans	3	9.2352	3134.97	-58.00		289	425	0.720	293
479	C8H16O2	isoamyl propionate								0.870	293
480	C8H16O2	isobutyl butyrate	1	-8.32597	1.42350	-4.25376	-3.09772	310	TC	0.863	291
481	C8H16O2	isobutyl isobutyrate	1	-8.18677	1.32200	-3.94343	-3.68833	310	TC	0.875	273
482	C8H16O2	n-propyl isovalerate								0.863	293
483	C8H18	n-octane	1	-7.91211	1.38007	-3.80435	-4.50132	260	TC	0.703	293
484	C8H18	2-methylheptane	1	-7.80701	1.38191	-3.78286	-3.50395	250	TC	0.702	289
485	C8H18	3-methylheptane	1	-7.82876	1.50656	-3.86146	-3.52377	255	TC	0.706	293
486	C8H18	4-methylheptane	1	-7.78757	1.40709	-3.76234	-3.50643	250	TC	0.705	293
487	C8H18	2,2-dimethylhexane	1	-7.69898	1.56083	-3.75189	-3.01869	245	TC	0.695	293
488	C8H18	2,3-dimethylhexane	1	-7.75180	1.58578	-3.80794	-2.58547	250	TC	0.712	293
489	C8H18	2,4-dimethylhexane	1	-7.65152	1.41393	-3.62789	-3.06548	245	TC	0.700	293
490	C8H18	2,5-dimethylhexane	1	-7.76508	1.51236	-3.78809	-3.07843	245	TC	0.693	293
491	C8H18	3,3-dimethylhexane	1	-7.59847	1.50336	-3.49912	-2.38236	245	TC	0.710	293
492	C8H18	3,4-dimethylhexane	1	-7.72976	1.61174	-3.75756	-2.62874	250	TC	0.719	293
493	C8H18	3-ethylhexane	1	-7.75246	1.42908	-3.68445	-3.46671	250	TC	0.718	289
494	C8H18	2,2,3-trimethylpentane	1	-7.48839	1.52208	-3.44481	-2.12538	245	TC	0.716	293
495	C8H18	2,2,4-trimethylpentane	1	-7.38890	1.25294	-3.16606	-2.22001	265	TC	0.692	293
496	C8H18	2,3,3-trimethylpentane	1	-7.41747	1.42778	-3.19166	-1.81367	245	TC	0.726	293
497	C8H18	2,3,4-trimethylpentane	1	-7.62000	1.60334	-3.57834	-2.04401	245	TC	0.719	293
498	C8H18	2-methyl-3-ethylpentane	1	-7.65393	1.54032	-3.64686	-2.52380	250	TC	0.719	293
499	C8H18	3-methyl-3-ethylpentane	1	-7.56484	1.58810	-3.40610	-1.71546	250	TC	0.727	293
500	C8H18	2,2,3,3-tetramethylbutane	3	11.4937	3856.39	-42.42		270	343		293

No	Formula	Name	MolWt	Tfp K	Tb K	Tc K	Pc bar	Vc cm³/mol	Zc	Omega	Dipm debye
501	C8H18O	1-octanol	130.231	257.7	468.3	652.5	28.6	490.	0.258	0.587	2.0
502	C8H18O	2-octanol	130.231	241.2	452.	637.					1.6
503	C8H18O	4-methyl-3-heptanol	130.231		443.	623.5					
504	C8H18O	5-methyl-3-heptanol	130.231		445.	621.2					
505	C8H18O	2-ethyl-1-hexanol	130.231	203.2	457.8	640.2					1.8
506	C8H18O	dibutyl ether	130.231	175.	413.4	580.	25.3			0.502	1.2
507	C8H18O	di-tert-butyl ether	130.231		382.2	550.	24.2				
508	C8H19N	dibutyl amine	129.247	211.	432.8	607.5	26.4			0.580	1.1
509	C8H19N	diisobutyl amine	129.247	203.	412.8	584.4	27.2			0.548	
510	C9H7N	quinoline	129.162	258.	510.8	782.					
511	C9H7N	isoquinoline	129.162	300.	516.4	803.					
512	C9H10	indane	118.179		451.1	684.9	39.5			0.308	
513	C9H10	alpha-methylstyrene	118.179		438.5	654.	34.				
514	C9H10O2	ethyl benzoate	150.178	238.3	485.9	668.7	23.2			0.48	
515	C9H12	n-propylbenzene	120.195	173.7	432.4	638.2	32.0	440.	0.265	0.344	
516	C9H12	isopropylbenzene	120.195	177.1	425.6	631.1	32.1			0.326	
517	C9H12	1-methyl-2-ethylbenzene	120.195	192.3	438.3	651.	30.4	460.	0.26	0.294	
518	C9H12	1-methyl-3-ethylbenzene	120.195	177.6	434.5	637.	28.4	490.	0.26	0.360	
519	C9H12	1-methyl-4-ethylbenzene	120.195	210.8	435.2	640.	29.4	470.	0.26	0.322	
520	C9H12	1,2,3-trimethylbenzene	120.195	247.7	449.3	664.5	34.5			0.366	
521	C9H12	1,2,4-trimethylbenzene	120.195	227.	442.5	649.2	32.3			0.376	0.1
522	C9H12	1,3,5-trimethylbenzene	120.195	228.4	437.9	637.3	31.3			0.399	
523	C9H13N	N,N-dimethyl-o-toluidine	135.210	212.	467.3	668.	31.2			0.484	0.9
524	C9H18	n-propylcyclohexane	126.243	178.7	429.9	639.0	28.0			0.258	
525	C9H18	isopropylcyclohexane	126.243	183.4	427.7	640.0	28.3			0.237	0.0

No	Formula	Name	CPVAP A	CPVAP B	CPVAP C	CPVAP D	DELHF	DELGF
501	C8H18O	1-octanol	6.171E+0	7.607E-1	-3.797E-4	6.263E-8	-3.601E+5	-1.202E+5
502	C8H18O	2-octanol	2.588E+1	7.641E-1	-4.224E-4	9.064E-8		
503	C8H18O	4-methyl-3-heptanol						
504	C8H18O	5-methyl-3-heptanol						
505	C8H18O	2-ethyl-1-hexanol	-1.499E+1	8.654E-1	-5.280E-4	1.285E-7	-3.655E+5	
506	C8H18O	dibutyl ether	6.054E+0	7.729E-1	-4.085E-4	8.085E-8	-3.341E+5	-8.859E+4
507	C8H18O	di-tert-butyl ether						
508	C8H19N	dibutyl amine	9.764E+0	8.081E-1	-4.392E-4	9.249E-8		
509	C8H19N	diisobutyl amine						
510	C9H7N	quinoline						
511	C9H7N	isoquinoline						
512	C9H10	indane						
513	C9H10	alpha-methylstyrene	-2.433E+1	6.933E-1	-4.530E-4	1.181E-7		
514	C9H1002	ethyl benzoate	-2.067E+1	6.887E-1	-3.608E-4	5.062E-8		
515	C9H12	n-propylbenzene	-3.129E+1	7.486E-1	-4.601E-4	1.081E-7	7.830E+3	1.373E+5
516	C9H12	isopropylbenzene	-3.936E+1	7.842E-1	-5.087E-4	1.291E-7	3.940E+3	1.371E+5
517	C9H12	1-methyl-2-ethylbenzene	-1.645E+1	6.996E-1	-4.120E-4	9.328E-8	1.210E+3	1.312E+5
518	C9H12	1-methyl-3-ethylbenzene	-2.900E+1	7.293E-1	-4.363E-4	9.998E-8	-1.930E+3	1.265E+5
519	C9H12	1-methyl-4-ethylbenzene	-2.731E+1	7.176E-1	-4.224E-4	9.542E-8	-2.050E+3	1.268E+5
520	C9H12	1,2,3-trimethylbenzene	-6.942E+0	6.335E-1	-3.326E-4	6.611E-8	-9.590E+3	1.246E+5
521	C9H12	1,2,4-trimethylbenzene	-4.668E+0	6.238E-1	-3.263E-4	6.376E-8	-1.394E+4	1.170E+5
522	C9H12	1,3,5-trimethylbenzene	-1.959E+1	6.724E-1	-3.692E-4	7.700E-8	-1.608E+4	1.180E+5
523	C9H13N	N,N-dimethyl-o-toluidine						
524	C9H18	n-propylcyclohexane						
525	C9H18	isopropylcyclohexane	-6.252E+1	9.889E-1	-5.795E-4	1.291E-7	-1.934E+5	4.735E+4

No	Formula	Name	Eq.	VP A	VP B	VP C	VP D	Tmin	Tmax	LDEN	TDEN
501	C8H18O	1-octanol	1	-9.71763	4.22514	-12.9222	-3.59254	325	TC	0.826	293
502	C8H18O	2-octanol	3	8.0906	2441.66	-150.7		345	453	0.821	293
503	C8H18O	4-methyl-3-heptanol									
504	C8H18O	5-methyl-3-heptanol									
505	C8H18O	2-ethyl-1-hexanol	3	8.7412	2773.46	-140.0		348	458	0.833	293
506	C8H18O	dibutyl ether	1	-9.04970	2.78734	-5.11686	-3.97104	362	TC	0.768	293
507	C8H18O	di-tert-butyl ether	1	-7.47062	1.33672	-4.00322	-1.89122	300	TC		
508	C8H19N	dibutyl amine	1	-9.14853	2.93179	-6.02092	0.93342	315	TC	0.767	293
509	C8H19N	diisobutyl amine	1	-8.95962	2.85335	-5.81427	0.65701	300	TC	0.741	298
510	C9H7N	quinoline	3	9.0779	3842.40	-86.94		437	515	1.095	293
511	C9H7N	isoquinoline	3	9.2957	3968.37	-88.94		437	517	1.091	303
512	C9H10	indane									
513	C9H10	alpha-methylstyrene	3	9.7106	3644.30	-67.15		348	493	0.911	293
514	C9H10O2	ethyl benzoate	1	-9.32936	2.89807	-6.54758	5.56703	317	TC	1.046	293
515	C9H12	n-propylbenzene	1	-7.92198	1.97403	-4.27504	-1.28568	346	TC	0.862	293
516	C9H12	isopropylbenzene	1	-7.46042	1.14486	-3.19082	-3.62628	343	TC	0.862	293
517	C9H12	1-methyl-2-ethylbenzene	1	-7.58007	2.20412	-6.68027	6.06587	354	TC	0.881	293
518	C9H12	1-methyl-3-ethylbenzene	1	-7.86301	2.47961	-6.98644	6.35609	351	TC	0.865	293
519	C9H12	1-methyl-4-ethylbenzene	1	-7.68892	1.92605	-5.51788	2.76399	351	TC	0.861	293
520	C9H12	1,2,3-trimethylbenzene	1	-8.44191	2.92198	-5.66712	2.28086	363	TC	0.894	293
521	C9H12	1,2,4-trimethylbenzene	1	-8.50002	2.98227	-6.02665	3.51307	358	TC	0.880	289
522	C9H12	1,3,5-trimethylbenzene	1	-8.37150	2.41166	-5.30321	2.67635	355	TC	0.865	293
523	C9H13N	N,N-dimethyl-o-toluidine								0.929	293
524	C9H18	n-propylcyclohexane	1	-7.37782	2.13149	-6.45979	5.82529	349	TC	0.793	293
525	C9H18	isopropylcyclohexane	1	-7.24565	2.09643	-6.35158	5.5038	344	TC	0.802	293

No	Formula	Name	MolWt	Tfp K	Tb K	Tc K	Pc bar	Vc cm^3/mol	Zc	Omega	Dipm debye
526	C9H18	1,trans-3,5-trimethylcyclohexane	126.243		413.7	602.2	23.4	580.	0.28	0.430	
527	C9H18	1-nonene	126.243	191.8	420.0	592.					
528	C9H18O	dibutyl ketone	142.242	267.3	461.6	640.					2.7
529	C9H20	n-nonane	128.259	219.7	424.0	594.6	22.9	548.	0.26	0.445	
530	C9H20	2-methyloctane	128.242	192.8	416.4	587.0	23.1			0.423	
531	C9H20	2,2-dimethylheptane	128.242	160.	405.9	576.8	23.5			0.390	
532	C9H20	2,2,3-trimethylhexane	128.259		406.8	588.	24.9			0.332	
533	C9H20	2,2,4-trimethylhexane	128.259	153.	399.7	573.7	23.7			0.321	
534	C9H20	2,2,5-trimethylhexane	128.259	167.4	397.2	568.	23.3	519.	0.260	0.357	
535	C9H20	3,3-diethylpentane	128.259	240.1	419.3	610.	26.7			0.338	0.0
536	C9H20	2,2,3,3-tetramethylpentane	128.259	263.	413.4	607.7	27.4			0.303	
537	C9H20	2,2,3,4-tetramethylpentane	128.259	152.	406.1	592.7	26.0			0.313	
538	C9H20	2,2,4,4-tetramethylpentane	128.259	206.0	395.4	574.7	24.9			0.312	
539	C9H20	2,3,3,4-tetramethylpentane	128.259	171.1	414.7	607.7	27.2			0.313	
540	C9H20O	1-nonanol	144.258	268.	486.7	671.		546.			1.7
541	C10F8	perfluoronaphthalene	272.094		482.	673.1	15.2			0.392	
542	C10F18	perfluorodecalin	462.074		415.	566.					
543	C10H8	naphthalene	128.174	353.5	491.1	748.4	40.5	413.	0.269	0.302	0.0
544	C10H12	1,2,3,4-tetrahydronaphthalene	132.206	242.	480.7	719.	35.1			0.303	
545	C10H14	n-butylbenzene	134.222	185.2	456.5	660.5	28.9	497.	0.261	0.393	0.4
546	C10H14	isobutylbenzene	134.222	221.7	445.9	650.	31.4	480.	0.28	0.380	0.3
547	C10H14	sec-butylbenzene	134.222	197.7	446.5	664.	29.4			0.274	0.4
548	C10H14	tert-butylbenzene	134.222	215.3	442.3	670.	29.6			0.265	0.5
549	C10H14	1-methyl-2-isopropylbenzene	134.222		451.5	666.	28.9			0.277	
550	C10H14	1-methyl-3-isopropylbenzene	134.222		448.3		29.3			0.279	

No	Formula	Name	CPVAP A	CPVAP B	CPVAP C	CPVAP D	DELHF	DELGF
526	C9H18	1,trans-3,5-trimethylcyclohexane	-3.718E+0	8.122E-1	-4.509E-4	9.705E-8	-1.036E+5	1.128E+5
527	C9H18	1-nonene						
528	C9H18O	dibutyl ketone						
529	C9H20	n-nonane	-8.374E+0	8.729E-1	-4.823E-4	1.031E-7	-2.292E+5	2.483E+4
530	C9H20	2-methyloctane	-1.011E+1	8.805E-1	-4.936E-4	1.083E-7	-2.292E+5	2.483E+4
531	C9H20	2,2-dimethylheptane	-2.089E+1	9.668E-1	-6.120E-4	1.570E-7	-2.470E+5	1.675E+4
532	C9H20	2,2,3-trimethylhexane	-4.563E+1	1.055E+0	-7.172E-4	1.987E-7	-2.414E+5	2.453E+4
533	C9H20	2,2,4-trimethylhexane	-6.031E+1	1.104E+0	-7.712E-4	2.188E-7	-2.434E+5	2.252E+4
534	C9H20	2,2,5-trimethylhexane	-5.411E+1	1.095E+0	-7.746E-4	2.255E-7	-2.542E+5	1.344E+4
535	C9H20	3,3-diethylpentane	-6.727E+1	1.126E+0	-7.988E-4	2.306E-7	-2.321E+5	3.509E+4
536	C9H20	2,2,3,3-tetramethylpentane	-5.458E+1	1.089E+0	-7.570E-4	2.142E-7	-2.374E+5	3.433E+4
537	C9H20	2,2,3,4-tetramethylpentane	-5.458E+1	1.089E+0	-7.570E-4	2.142E-7	-2.371E+5	3.266E+4
538	C9H20	2,2,4,4-tetramethylpentane	-6.740E+1	1.168E+0	-8.612E-4	2.574E-7	-2.421E+5	3.404E+4
539	C9H20	2,3,3,4-tetramethylpentane	-5.492E+1	1.091E+0	-7.603E-4	2.158E-7	-2.364E+5	3.412E+4
540	C9H20O	1-nonanol	1.280E+0	8.817E-1	-4.791E-4	9.801E-8	-3.872E+5	-1.183E+5
541	C10F8	perfluoronaphthalene						
542	C10F18	perfluorodecalin						
543	C10H8	naphthalene	-6.880E+1	8.499E-1	-6.506E-4	1.981E-7	1.511E+5	2.237E+5
544	C10H12	1,2,3,4-tetrahydronaphthalene					2.760E+3	1.671E+5
545	C10H14	n-butylbenzene	-2.299E+1	7.934E-1	-4.396E-4	8.570E-8	-1.382E+4	1.448E+5
546	C10H14	isobutylbenzene	-6.515E+1	9.893E-1	-7.214E-4	2.152E-7	-2.156E+4	
547	C10H14	sec-butylbenzene	-8.600E+1	1.102E+0	-8.746E-4	2.827E-7	-1.746E+4	
548	C10H14	tert-butylbenzene					-2.269E+4	
549	C10H14	1-methyl-2-isopropylbenzene						
550	C10H14	1-methyl-3-isopropylbenzene	-4.876E+1	9.064E-1	-6.054E-4	1.627E-7	-2.931E+4	

No	Formula	Name	Eq.	VP A	VP B	VP C	VP D	Tmin	Tmax	LDEN	TDEN
526	C9H18	1,trans-3,5-trimethylcyclohexane								0.722	293
527	C9H18	1-nonene	1	-8.30824	2.03357	-5.42753	0.95331	340	TC	0.745	273
528	C9H18O	dibutyl ketone								0.827	286
529	C9H20	n-nonane	1	-8.24480	1.57885	-4.38155	-4.04412	343	TC	0.718	293
530	C9H20	2-methyloctane	3	9.3089	3246.64	-67.20		323	448	0.713	293
531	C9H20	2,2-dimethylheptane	3	9.1710	3120.00	-65.20		313	438	0.711	293
532	C9H20	2,2,3-trimethylhexane	3	9.1815	3164.17	-61.66		297	436	0.729	293
533	C9H20	2,2,4-trimethylhexane	3	9.1437	3084.08	-61.94		291	428	0.720	289
534	C9H20	2,2,5-trimethylhexane	1	-7.80573	1.68023	-4.50859	-0.78808	319	TC	0.717	289
535	C9H20	3,3-diethylpentane	1	-7.98732	2.15446	-4.25035	-0.09787	336	TC	0.752	293
536	C9H20	2,2,3,3-tetramethylpentane	1	-7.40615	1.23976	-2.94462	-3.35833	331	TC	0.757	293
537	C9H20	2,2,3,4-tetramethylpentane	1	-7.60624	1.62208	-3.71777	-1.50403	325	TC	0.739	293
538	C9H20	2,2,4,4-tetramethylpentane	1	-7.71570	1.89775	-4.08940	-0.75421	316	TC	0.719	293
539	C9H20	2,3,3,4-tetramethylpentane	1	-7.65000	1.71897	-3.82026	-0.95911	332	TC	0.755	293
540	C9H20O	1-nonanol	3	8.7513	2939.54	-150.1		363	487	0.828	293
541	C10F8	perfluoronaphthalene									
542	C10F18	perfluorodecalin									
543	C10H8	naphthalene	1	-7.85178	2.17172	-3.70504	-4.81238	399	TC	0.971	363
544	C10H12	1,2,3,4-tetrahydronaphthalene	3	9.5883	4009.49	-64.89		365	500	0.973	293
545	C10H14	n-butylbenzene	1	-8.39978	2.61916	-5.80532	2.11591	369	TC	0.860	293
546	C10H14	isobutylbenzene	1	-8.13153	1.58186	-2.37146	-7.46781	360	TC	0.853	293
547	C10H14	sec-butylbenzene	1	-7.49482	2.23440	-6.77346	6.31118	360	TC	0.862	293
548	C10H14	tert-butylbenzene	1	-7.45802	2.33227	-7.07129	6.72178	357	TC	0.867	293
549	C10H14	1-methyl-2-isopropylbenzene	3	9.3607	3564.52	-70.00		330	481	0.876	293
550	C10H14	1-methyl-3-isopropylbenzene	2	61.106	8033.58	-7.076	6293.	330	TC	0.861	293

No	Formula	Name	MolWt	Tfp K	Tb K	Tc K	Pc bar	Vc cm^3/mol	Zc	Omega	Dipm debye
551	C10H14	1-methyl-4-isopropylbenzene	134.222	200.	450.3	651.	27.3			0.373	0.0
552	C10H14	1,4-diethylbenzene	134.222	231.	456.9	657.9	28.0			0.404	0.1
553	C10H14	1,2,3,5-tetramethylbenzene	134.222	249.	471.2	679.					
554	C10H14	1,2,4,5-tetramethylbenzene	134.212	352.	470.0	675.	29.4			0.435	
555	C10H14O	thymol	150.221	323.	505.7	698.					
556	C10H15N	n-butylaniline	149.236	259.	513.9	721.	28.3			0.286	0.0
557	C10H18	cis-decalin	138.254	230.	468.9	702.3	32.0			0.270	0.0
558	C10H18	trans-decalin	138.254	242.8	460.5	687.1	31.4				
559	C10H18	1,3-decadiene	138.254		442.	615.					
560	C10H19N	caprylonitrile	153.269	255.3	516.	622.0	32.5				
561	C10H20	butylcyclohexane	140.260	198.4	454.1	667.	31.5			0.362	
562	C10H20	isobutylcyclohexane	140.270		444.5	659.	31.2			0.319	
563	C10H20	sec-butylcyclohexane	140.270		452.5	669.	26.7			0.264	
564	C10H20	tert-butylcyclohexane	140.270	232.0	444.7	659.	26.6			0.252	
565	C10H20	1-decene	140.270	206.9	443.7	615.	22.0	650.	0.28	0.491	0.0
566	C10H20O	menthol	156.269	316.	489.5	694.					
567	C10H22	n-decane	142.286	243.5	447.3	617.7	21.2	603.	0.249	0.489	0.0
568	C10H22	3,3,5-trimethylheptane	142.286		428.9	609.7	23.2			0.382	
569	C10H22	2,2,3,3-tetramethylhexane	142.286		433.5	623.2	25.1			0.364	
570	C10H22	2,2,5,5-tetramethylhexane	142.286		410.6	581.6	21.9			0.375	
571	C10H22O	1-decanol	158.285	280.1	506.1	687.	22.2	600.	0.230	0.310	1.8
572	C11H10	1-methylnaphthalene	142.201	242.7	517.9	772.	36.	462.	0.234	0.382	0.5
573	C11H10	2-methylnaphthalene	142.201	307.7	514.3	761.	35.	462.	0.26		0.4
574	C11H14O2	butyl benzoate	178.232	251.	523.	723.	26.	561.	0.25	0.58	
575	C11H16	pentamethylbenzene	148.249	327.5	504.6	719.					

No	Formula	Name	CPVAP A	CPVAP B	CPVAP C	CPVAP D	DELHF	DELGF
551	C10H14	1-methyl-4-isopropylbenzene	-3.742E+1	8.671E-1	-5.560E-4	1.411E-7	-2.227E+4	1.380E+5
552	C10H14	1,4-diethylbenzene	3.923E+0	7.131E-1	-3.711E-4	6.840E-8	-4.484E+4	1.188E+5
553	C10H14	1,2,3,5-tetramethylbenzene	1.652E+1	6.519E-1	-2.879E-4	3.257E-8	-4.530E+4	1.195E+5
554	C10H14	1,2,4,5-tetramethylbenzene						
555	C10H14O	thymol						
556	C10H15N	n-butylaniline	-3.407E+1	9.144E-1	-5.560E-4	1.287E-7		
557	C10H18	cis-decalin	-1.125E+2	1.118E+0	-6.607E-4	1.437E-7	-1.691E+5	8.587E+4
558	C10H18	trans-decalin	-9.767E+1	1.045E+0	-5.476E-4	8.981E-8	-1.824E+5	7.348E+4
559	C10H18	1,3-decadiene						
560	C10H19N	caprylonitrile						
561	C10H20	butylcyclohexane	-6.296E+1	1.081E+0	-6.305E-4	1.400E-7	-2.133E+5	5.648E+4
562	C10H20	isobutylcyclohexane						
563	C10H20	sec-butylcyclohexane						
564	C10H20	tert-butylcyclohexane						
565	C10H20	1-decene	-4.664E+0	9.077E-1	-5.058E-4	1.095E-7	-1.242E+5	1.211E+5
566	C10H20O	menthol						
567	C10H22	n-decane	-7.913E+0	9.609E-1	-5.288E-4	1.131E-7	-2.498E+5	3.324E+4
568	C10H22	3,3,5-trimethylheptane	-7.037E+1	1.232E+0	-8.646E-4	2.455E-7	-2.587E+5	3.358E+4
569	C10H22	2,2,3,3-tetramethylhexane	-5.883E+1	1.231E+0	-8.834E-4	2.585E-7		
570	C10H22	2,2,5,5-tetramethylhexane	-6.234E+1	1.245E+0	-8.956E-4	2.618E-7		
571	C10H22O	1-decanol	1.457E+1	8.947E-1	-3.921E-4	3.451E-8	-4.019E+5	-1.043E+5
572	C11H10	1-methylnaphthalene	-6.482E+1	9.387E-1	-6.942E-4	2.016E-7	1.169E+5	2.178E+5
573	C11H10	2-methylnaphthalene	-5.652E+1	8.997E-1	-6.469E-4	1.840E-7	1.162E+5	2.163E+5
574	C11H14O2	butyl benzoate	-1.737E+1	8.675E-1	-4.610E-4	7.235E-8		
575	C11H16	pentamethylbenzene						

No	Formula	Name	Eq.	VP A	VP B	VP C	VP D	Tmin	Tmax	LDEN	TDEN
551	C10H14	1-methyl-4-isopropylbenzene	2	56.605	7800.97	-6.432	6308.	360	TC	0.857	293
552	C10H14	1,4-diethylbenzene	1	-8.11413	1.77697	-4.43960	-1.47477	370	TC	0.862	293
553	C10H14	1,2,3,5-tetramethylbenzene	3	9.6750	3854.53	-72.26		368	513	0.890	293
554	C10H14	1,2,4,5-tetramethylbenzene	2	57.519	8300.92	-6.478	6600.	360	TC	0.838	354
555	C10H14O	thymol									
556	C10H15N	n-butylaniline	3	9.7792	4079.72	-96.15		385	560	0.932	293
557	C10H18	cis-decalin	3	9.2110	3671.61	-69.74		368	495	0.897	293
558	C10H18	trans-decalin	3	9.1787	3610.66	-66.49		363	470	0.870	293
559	C10H18	1,3-decadiene								0.750	293
560	C10H19N	caprylonitrile								0.820	293
561	C10H20	butylcyclohexane	3	9.2914	3542.57	-72.32		332	485	0.799	293
562	C10H20	isobutylcyclohexane	1	-8.05035	2.67134	-5.49473	2.06044	358	TC	0.795	293
563	C10H20	sec-butylcyclohexane	1	-7.49250	2.47712	-7.51526	7.69513	369	TC	0.813	293
564	C10H20	tert-butylcyclohexane	1	-7.34348	2.13810	-6.48025	5.89241	357	TC	0.813	293
565	C10H20	1-decene	1	-9.05778	3.06154	-7.07236	4.20695	360	TC	0.741	293
566	C10H20O	menthol									
567	C10H22	n-decane	1	-8.56523	1.97756	-5.81971	-0.29982	368	TC	0.730	293
568	C10H22	3,3,5-trimethylheptane	3	9.1646	3305.20	-67.66		313	458		
569	C10H22	2,2,3,3-tetramethylhexane	3	9.1396	3371.05	-64.09		314	463		
570	C10H22	2,2,5,5-tetramethylhexane	3	9.2244	3172.92	-66.15		300	438		
571	C10H22O	1-decanol	1	-8.62283	1.39315	-8.24774	-19.21149	400	TC	0.830	293
572	C11H10	1-methylnaphthalene	1	-7.56390	1.19577	-3.38134	-2.86388	415	TC	1.020	293
573	C11H10	2-methylnaphthalene	1	-8.43595	2.88433	-5.70017	2.50897	412	TC	0.990	313
574	C11H14O2	butyl benzoate	3	9.7161	4158.47	-94.15		390	570	1.006	293
575	C11H16	pentamethylbenzene	3	9.8147	4222.48	-74.20		398	543		

No	Formula	Name	MolWt	Tfp K	Tb K	Tc K	Pc bar	Vc cm³/mol	Zc	Omega	Dipm debye
576	C11H22	n-hexylcyclopentane	154.297	200.2	476.3	660.1	21.3			0.476	
577	C11H22	1-undecene	154.297	224.0	465.8	637.	19.9			0.518	
578	C11H24	n-undecane	156.313	247.6	469.1	638.8	19.7	660.	0.24	0.535	0.0
579	C12H10	diphenyl	154.212	342.4	529.3	789.	38.5	502.	0.295	0.372	
580	C12H10O	diphenyl ether	170.211	300.	531.2	766.	31.4			0.44	1.1
581	C12H18	hexamethylbenzene	162.276		536.6	758.				0.515	
582	C12H24	n-heptylcyclopentane	168.324	220.	497.3	679.	19.4			0.558	
583	C12H24	1-dodecene	168.324	238.0	486.5	657.	18.5				
584	C12H26	dodecane	170.340	263.6	489.5	658.2	18.2	713.	0.24	0.575	0.0
585	C12H26O	dihexyl ether	186.339	230.0	499.6	657.	18.2	720.	0.24	0.70	
586	C12H26O	dodecanol	186.339	297.1	533.1	679.	19.2	718.	0.24		1.6
587	C12H27N	tributylamine	185.355		486.6	643.	18.2				0.8
588	C13H12	diphenylmethane	168.239	300.	538.2	770.	28.6			0.442	0.4
589	C13H26	n-octylcyclopentane	182.351	229.	516.9	694.	17.9			0.564	
590	C13H26	1-tridecene	182.351	250.1	505.9	674.	17.0			0.598	
591	C13H28	n-tridecane	184.367	267.8	508.6	676.	17.2	780.	0.240	0.619	0.0
592	C14H10	anthracene	178.234	489.7	613.1	869.3		554.			
593	C14H10	phenanthrene	178.234	373.7	613.	873.		554.			0.0
594	C14H28	n-nonylcyclopentane	196.378	244.	535.3	710.5	16.5			0.610	
595	C14H28	1-tetradecene	196.378	260.3	524.3	689.	15.6			0.644	
596	C14H30	n-tetradecane	198.394	279.0	526.7	693.0	14.4	830.	0.23	0.581	0.0
597	C15H30	n-decylcyclopentane	210.405	251.1	552.5	723.8	15.2			0.654	
598	C15H30	1-pentadecene	210.405	269.4	541.5	704.	14.5			0.682	
599	C15H32	n-pentadecane	212.421	283.	543.8	707.	15.2	880.	0.23	0.706	
600	C16H22O4	dibutyl-o-phthalate	278.350	238.	608.						

No	Formula	Name	CPVAP A	CPVAP B	CPVAP C	CPVAP D	DELHF	DELGF
576	C11H22	n-hexylcyclopentane	-5.832E+1	1.128E+0	-6.536E-4	1.473E-7	-2.096E+5	7.825E+4
577	C11H22	1-undecene	-5.585E+0	1.003E+0	-5.602E-4	1.216E-7	-1.449E+5	1.295E+5
578	C11H24	n-undecane	-8.395E+0	1.054E+0	-5.799E-4	1.237E-7	-2.705E+5	4.162E+4
579	C12H10	diphenyl	-9.707E+1	1.106E+0	-8.855E-4	2.790E-7	1.822E+5	2.803E+5
580	C12H10O	diphenyl ether	-6.073E+1	9.282E-1	-5.870E-4	1.359E-7	4.999E+4	
581	C12H18	hexamethylbenzene	-5.926E+1	1.223E+0	-7.084E-4	1.596E-7		
582	C12H24	n-heptylcyclopentane	-6.544E+0	1.098E+0	-6.155E-4	1.341E-7	-2.303E+5	8.667E+4
583	C12H24	1-dodecene	-9.328E+0	1.149E+0	-6.347E-4	1.359E-7	-1.655E+5	1.380E+5
584	C12H26	dodecane	3.354E+1	1.073E+0	-5.535E-4	1.678E-7	-2.911E+5	5.007E+4
585	C12H26O	dihexyl ether						
586	C12H26O	dodecanol	9.224E+0	1.103E+0	-5.338E-4	7.779E-8	-4.431E+5	-8.713E+4
587	C12H27N	tributylamine	7.993E+0	1.198E+0	-6.703E-4	1.449E-7		
588	C13H12	diphenylmethane						
589	C13H26	n-octylcyclopentane	-5.995E+1	1.317E+0	-7.612E-4	1.708E-7	-2.509E+5	9.512E+4
590	C13H26	1-tridecene	-7.118E+0	1.191E+0	-6.674E-4	1.451E-7	-1.861E+5	1.464E+5
591	C13H28	n-tridecane	-1.046E+1	1.245E+0	-6.912E-4	1.490E-7	-3.117E+5	5.849E+4
592	C14H10	anthracene	-5.898E+1	1.006E+0	-6.594E-4	1.606E-7	2.248E+5	
593	C14H10	phenanthrene	-5.898E+1	1.006E+0	-6.594E-4	1.606E-7		
594	C14H28	n-nonylcyclopentane	-6.081E+1	1.412E+0	-8.156E-4	1.830E-7	-2.715E+5	1.035E+5
595	C14H28	1-tetradecene	-7.967E+0	1.286E+0	-7.210E-4	1.569E-7	-2.067E+5	1.549E+5
596	C14H30	n-tetradecane	-1.098E+1	1.338E+0	-7.423E-4	1.598E-7	-3.323E+5	6.686E+4
597	C15H30	n-decylcyclopentane	-6.192E+1	1.508E+0	-8.717E-4	1.959E-7	-2.922E+5	1.119E+5
598	C15H30	1-pentadecene	-9.203E+0	1.382E+0	-7.783E-4	1.703E-7	-2.274E+5	1.632E+5
599	C15H32	n-pentadecane	-1.192E+1	1.433E+0	-7.972E-4	1.720E-7	-3.530E+5	7.528E+4
600	C16H22O4	dibutyl-o-phthalate	1.880E+0	1.254E+0	-6.121E-4	6.971E-8		

No	Formula	Name	Eq.	VP A	VP B	VP C	VP D	Tmin	Tmax	LDEN	TDEN
576	C11H22	n-hexylcyclopentane	3	9.3938	3702.56	-81.55		351	507	0.797	293
577	C11H22	1-undecene	2	71.675	9105.75	-8.489	8596.	350	TC	0.751	293
578	C11H24	n-undecane	2	73.501	9305.80	-8.729	8813.	350	TC	0.740	293
579	C12H10	diphenyl	1	-7.67400	1.23008	-3.67908	-2.29172	342	TC	0.990	347
580	C12H10O	diphenyl ether	1	-8.59849	2.46297	-5.62029	-1.23996	477	TC	1.066	303
581	C12H18	hexamethylbenzene									
582	C12H24	n-heptylcyclopentane	3	9.4387	3850.38	-88.75		368	529	0.810	293
583	C12H24	1-dodecene	2	76.348	9846.99	-9.073	9826.	360	TC	0.758	293
584	C12H26	dodecane	2	77.628	10012.5	-9.236	10030.	360	TC	0.748	293
585	C12H26O	dihexylether	3	9.7170	3982.78	-89.15		373	545	0.794	293
586	C12H26O	dodecanol	3	8.6436	3242.04	-157.1		407	580	0.835	293
587	C12H27N	tributylamine	3	9.6676	3865.58	-86.15		362	531	0.779	293
588	C13H12	diphenylmethane	3	7.8654	2902.44	-167.9		473	563	1.006	293
589	C13H26	n-octylcyclopentane	3	9.4739	3983.01	-95.85		385	549	0.805	293
590	C13H26	1-tridecene	2	81.389	10609.4	-9.709	11250.	370	TC	0.766	293
591	C13H28	n-tridecane	3	9.5153	3892.91	-98.93		380	540	0.756	293
592	C14H10	anthracene	3	11.0499	6492.44	-26.13		490	655		
593	C14H10	phenanthrene	3	10.0985	5477.94	-69.39		450	655		
594	C14H28	n-nonylcyclopentane	3	9.4887	4096.30	-103.0		400	569	0.808	293
595	C14H28	1-tetradecene	2	85.854	11329.2	-10.27	12800.	380	TC	0.786	273
596	C14H30	n-tetradecane	2	84.552	11322.9	-10.07	12500.	380	TC	0.763	293
597	C15H30	n-decylcyclopentane	3	9.5059	4203.94	-109.7		413	586	0.811	293
598	C15H30	1-pentadecene	2	92.300	12205.3	-11.09	14370.	400	TC	0.791	273
599	C15H32	n-pentadecane	2	88.380	11995.6	-10.54	13840.	400	TC	0.769	273
600	C16H22O4	dibutyl-o-phthalate	3	10.3337	4852.47	-138.1		469	657	1.047	293

No	Formula	Name	MolWt	Tfp K	Tb K	Tc K	Pc bar	Vc cm³/mol	Zc	Omega	Dipm debye
601	C16H32	n-decylcyclohexane	224.432	271.	570.8	750.	13.5			0.583	
602	C16H32	1-hexadecene	224.432	277.3	558.	717.	13.3			0.721	
603	C16H34	hexadecane	226.448	291.	560.	722.	14.1			0.742	
604	C17H34	n-dodecylcyclopentane	238.459	268.	584.1	750.	12.9			0.719	
605	C17H36O	heptadecanol	256.474	327.	597.	736.	14.1				
606	C17H36	n-heptadecane	240.475	295.	575.2	733.	13.	1000.	0.22	0.77	
607	C18H14	o-terphenyl	230.310	330.	605.	891.0	39.0	753.	0.396	0.431	
608	C18H14	m-terphenyl	230.310	360.	638.	924.9	35.1	768.	0.358	0.449	
609	C18H14	p-terphenyl	230.310	485.	649.	926.0	33.2	763.	0.329	0.523	0.7
610	C18H36	1-octadecene	252.486	290.8	588.0	739.	11.3			0.807	
611	C18H36	n-tridecylcyclopentane	252.486	278.	598.6	761.	12.0			0.755	
612	C18H38	octadecane	254.504	301.3	589.5	748.	12.0			0.790	
613	C18H38O	1-octadecanol	270.501	331.	608.	747.	14.1				1.7
614	C19H38	1-cyclopentyltetradecane	266.513	282.	599.	772.	11.2			0.789	
615	C19H40	n-nonadecane	268.529	305.	603.1	756.	11.1			0.827	
616	C20H40	1-cyclopentylpentadecane	280.540	290.	625.	780.	10.2			0.833	
617	C20H42	n-eicosane	282.556	310.	617.	767.	11.1			0.907	
618	C20H42O	1-eicosanol	298.555	339.	629.	770.	12.				

No	Formula	Name	CPVAP A	CPVAP B	CPVAP C	CPVAP D	DELHF	DELGF
601	C16H32	n-decylcyclohexane	-6.902E+1	1.654E+0	-9.613E-4	2.143E-7		
602	C16H32	1-hexadecene	-9.705E+0	1.475E+0	-8.298E-4	1.810E-7	-2.480E+5	1.716E+5
603	C16H34	hexadecane	-1.302E+1	1.529E+0	-8.537E-4	1.850E-7	-3.736E+5	8.374E+4
604	C17H34	n-dodecylcyclopentane	-6.326E+1	1.695E+0	-9.768E-4	2.186E-7	-3.361E+5	1.260E+5
605	C17H36O	heptadecanol	-7.792E+0	1.653E+0	-9.345E-4	2.044E-7	-5.463E+5	-4.467E+4
606	C17H36	n-heptadecane	-1.397E+1	1.624E+0	-9.081E-4	1.972E-7	-3.942E+5	9.215E+4
607	C18H14	o-terphenyl						
608	C18H14	m-terphenyl						
609	C18H14	p-terphenyl						
610	C18H36	1-octadecene	-1.133E+1	1.664E+0	-9.374E-4	2.049E-7	-2.892E+5	1.884E+5
611	C18H36	n-tridecylcyclopentane	-6.421E+1	1.790E+0	-1.032E-3	2.309E-7	-3.540E+5	1.371E+5
612	C18H38	octadecane	-1.447E+1	1.717E+0	-9.592E-4	2.078E-7	-4.148E+5	1.006E+5
613	C18H38O	1-octadecanol	-8.704E+0	1.748E+0	-9.881E-4	2.157E-7	-5.669E+5	-3.622E+4
614	C19H38	1-cyclopentyltetradecane	-6.493E+1	1.884E+0	-1.085E-3	2.426E-7	-3.746E+5	1.456E+5
615	C19H40	n-nonadecane	-1.549E+1	1.812E+0	-1.015E-3	2.205E-7	-4.354E+5	1.090E+5
616	C20H40	1-cyclopentylpentadecane	-6.609E+1	1.980E+0	-1.140E-3	2.550E-7	-3.953E+5	1.540E+5
617	C20H42	n-eicosane	-2.238E+1	1.939E+0	-1.117E-3	2.528E-7	-4.561E+5	1.174E+5
618	C20H42O	1-eicosanol	-1.258E+1	1.950E+0	-1.118E-3	2.516E-7	-6.081E+5	-1.943E+4

No	Formula	Name	Eq.	VP A	VP B	VP C	VP D	Tmin	Tmax	LDEN	TDEN
601	C16H32	n-decylcyclohexane	3	9.5425	4373.37	-111.8		463	573	0.819	293
602	C16H32	1-hexadecene	2	99.280	13117.0	-11.99	16260.	400	TC	0.788	283
603	C16H34	hexadecane	2	89.060	12411.3	-10.58	15200.	400	TC	0.773	293
604	C17H34	n-dodecylcyclopentane	3	9.5713	4395.87	-124.2		441	619	0.816	293
605	C17H36O	heptadecanol	3	8.9959	3672.62	-188.1		464	656	0.848	327
606	C17H36	n-heptadecane	3	9.5308	4294.55	-124.0		434	610	0.778	298
607	C18H14	o-terphenyl									
608	C18H14	m-terphenyl									
609	C18H14	p-terphenyl									
610	C18H36	1-octadecene	3	9.6019	4416.13	-127.3		444	623	0.789	293
611	C18H36	n-tridecylcyclopentane	3	9.6068	4483.13	-131.3		453	634	0.818	293
612	C18H38	octadecane	3	9.5030	4361.79	-129.9		445	625	0.777	301
613	C18H38O	1-octadecanol	3	9.0696	3757.82	-193.1		474	658	0.812	332
614	C19H38	1-cyclopentyltetradecane	3	9.6430	4439.38	-138.1		465	648	0.820	293
615	C19H40	n-nonadecane	3	9.5331	4450.44	-135.6		456	639	0.789	305
616	C20H40	1-cyclopentylpentadecane	3	9.6890	4692.01	-145.1		476	661	0.821	293
617	C20H42	n-eicosane	3	9.8483	4680.46	-141.1		471	652	0.775	313
618	C20H42O	1-eicosanol	3	9.2031	3912.10	-203.1		492	679		

Lennard-Jones Potentials as Determined from Viscosity Data[†]

Substance		b_0,[‡] cm³/g-mol	σ, Å	ϵ/k, K
Ar	Argon	56.08	3.542	93.3
He	Helium	20.95	2.551[§]	10.22
Kr	Krypton	61.62	3.655	178.9
Ne	Neon	28.30	2.820	32.8
Xe	Xenon	83.66	4.047	231.0
Air	Air	64.50	3.711	78.6
AsH₃	Arsine	89.88	4.145	259.8
BCl₃	Boron chloride	170.1	5.127	337.7
BF₃	Boron fluoride	93.35	4.198	186.3
B(OCH₃)₃	Methyl borate	210.3	5.503	396.7
Br₂	Bromine	100.1	4.296	507.9
CCl₄	Carbon tetrachloride	265.5	5.947	322.7
CF₄	Carbon tetrafluoride	127.9	4.662	134.0
CHCl₃	Chloroform	197.5	5.389	340.2
CH₂Cl₂	Methylene chloride	148.3	4.898	356.3
CH₃Br	Methyl bromide	88.14	4.118	449.2
CH₃Cl	Methyl chloride	92.31	4.182	350
CH₃OH	Methanol	60.17	3.626	481.8
CH₄	Methane	66.98	3.758	148.6
CO	Carbon monoxide	63.41	3.690	91.7
COS	Carbonyl sulfide	88.91	4.130	336.0
CO₂	Carbon dioxide	77.25	3.941	195.2
CS₂	Carbon disulfide	113.7	4.483	467
C₂H₂	Acetylene	82.79	4.033	231.8
C₂H₄	Ethylene	91.06	4.163	224.7
C₂H₆	Ethane	110.7	4.443	215.7
C₂H₅Cl	Ethyl chloride	148.3	4.898	300
C₂H₅OH	Ethanol	117.3	4.530	362.6
C₂N₂	Cyanogen	*104.7*	*4.361*	*348.6*
CH₃OCH₃	Methyl ether	100.9	4.307	395.0

Substance		b_0,‡ cm³/g-mol	σ, Å	ϵ/k, K
CH_2CHCH_3	Propylene	129.2	4.678	298.9
CH_3CCH	Methylacetylene	136.2	4.761	251.8
C_3H_6	Cyclopropane	140.2	4.807	248.9
C_3H_8	Propane	169.2	5.118	237.1
$n\text{-}C_3H_7OH$	n-Propyl alcohol	118.8	4.549	576.7
CH_3COCH_3	Acetone	122.8	4.600	560.2
CH_3COOCH_3	Methyl acetate	151.8	4.936	469.8
$n\text{-}C_4H_{10}$	n-Butane	130.0	4.687	531.4
$iso\text{-}C_4H_{10}$	Isobutane	185.6	5.278	330.1
$C_2H_5OC_2H_5$	Ethyl ether	231.0	5.678	313.8
$CH_3COOC_2H_5$	Ethyl acetate	178.0	5.205	521.3
$n\text{-}C_5H_{12}$	n-Pentane	244.2	5.784	341.1
$C(CH_3)_4$	2,2-Dimethylpropane	340.9	6.464	193.4
C_6H_6	Benzene	193.2	5.349	412.3
C_6H_{12}	Cyclohexane	298.2	6.182	297.1
$n\text{-}C_6H_{14}$	n-Hexane	265.7	5.949	399.3
Cl_2	Chlorine	94.65	4.217	316.0
F_2	Fluorine	47.75	3.357	112.6
HBr	Hydrogen bromide	47.58	3.353	449
HCN	Hydrogen cyanide	60.37	3.630	569.1
HCl	Hydrogen chloride	46.98	3.339	344.7
HF	Hydrogen fluoride	39.37	3.148	330
HI	Hydrogen iodide	94.24	4.211	288.7
H_2	Hydrogen	28.51	2.827	59.7
H_2O	Water	23.25	2.641	809.1
H_2O_2	Hydrogen peroxide	93.24	4.196	289.3
H_2S	Hydrogen sulfide	60.02	3.623	301.1
Hg	Mercury	33.03	2.969	750
$HgBr_2$	Mercuric bromide	165.5	5.080	686.2
$HgCl_2$	Mercuric chloride	118.9	4.550	750
HgI_2	Mercuric iodide	224.6	5.625	695.6
I_2	Iodine	173.4	5.160	474.2
NH_3	Ammonia	30.78	2.900	558.3
NO	Nitric oxide	53.74	3.492	116.7
$NOCl$	Nitrosyl chloride	87.75	4.112	395.3
N_2	Nitrogen	69.14	3.798	71.4
N_2O	Nitrous oxide	70.80	3.828	232.4
O_2	Oxygen	52.60	3.467	106.7
PH_3	Phosphine	79.63	3.981	251.5
SF_6	Sulfur hexafluoride	170.2	5.128	222.1
SO_2	Sulfur dioxide	87.75	4.112	335.4
SiF_4	Silicon tetrafluoride	146.7	4.880	171.9
SiH_4	Silicon hydride	85.97	4.084	207.6
$SnBr_4$	Stannic bromide	329.0	6.388	563.7
UF_6	Uranium hexafluoride	268.1	5.967	236.8

†R. A. Svehla, *NASA Tech. Rep.* R-132, Lewis Research Center, Cleveland, Ohio, 1962.
‡$b_0 = \frac{2}{3}\pi N_0 \sigma^3$, where N_0 is Avogadro's number.
§The parameter σ was determined by quantum-mechanical formulas.

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